Reactions of diazoalkanes with unsaturated compounds
15.* Catalytic reactions of unsaturated carbonyl compounds and their derivatives with diazomethane**

M. D. Khanova,[a] R. M. Sultanova,[a] S. S. Zlotskii,[a] V. A. Dokichev,[a] and Yu. V. Tomilov[b]*

[a]*Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066. E-mail: dokichev@anrb.ru*
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 6390. E-mail: tom@ioc.ac.ru*

The present study concerned with the influence of the nature of the acetal fragment in unsaturated compounds on the reactivity of the C=C bond in cyclopropanation reactions with diazomethane catalyzed by copper and palladium compounds. The acetal substituents at the α- or γ-position with respect to the C=C bond were found to exert an activating effect on the yields of cyclopropanation products compared to the starting unsaturated carbonyl compounds, which give 1,3-dipolar cycloaddition adducts with CH_2N_2 as by-products. Cyclopropanation of the double bonds appeared to be most efficiently catalyzed by $Pd(acac)_2$.

Key words: unsaturated carbonyl compounds, acetals, 1,3-dioxolanes, diazomethane, cyclopropanes, metal complex catalysis, cyclopropanation.

Aldehydes of the cyclopropane series are of interest as synthons for the synthesis of biologically active polyfunctional compounds,[2—6] for example, of 5,6-methanoleukotriene A_4, which is a stable and selective inhibitor of the biosynthesis of leukotriene,[7] as well as for the production of fragrance compounds for perfumery, such as 5-(2,2-dimethylcyclopropyloct-3-methylpent-2-enal (citral-6,7-cyclopropane).[8]

It has been demonstrated[9,10] that the introduction of the oxazolidine or boronate group into unsaturated compounds leads to an increase in both the yields of cyclopropanation products compared to those obtained in reactions with unfunctionalized molecules and the regioselectivity of cyclopropanation of dienes with CH_2N_2 in the presence of $Pd(acac)_2$. The influence of the nature of the acetal substituents in olefins on catalytic reactions of the latter with CH_2N_2 has not been previously examined. It should be noted that the reactions of methyl diazoacetate with cyclic acetals, *viz.*, 2-substituted 1,3-dioxanes, in the presence of copper or rhodium compounds are accompanied by the introduction of methoxycarbonylcarbene at the C—O bond of dioxolane to form esters of 3-substituted 1,4-dioxepane-2-carboxylic acids.[11]

In the present study, we examined the influence of the nature of the acetal group and the catalyst on catalytic cyclopropanation of a series of unsaturated compounds, such as *trans*-crotonaldehyde (**1a**), *trans*-cinnamaldehyde (**2a**), hex-5-en-2-one (**3a**), and their acyclic (**1b—3b**) and cyclic (**1c,d—3c,d**) derivatives, with diazomethane.

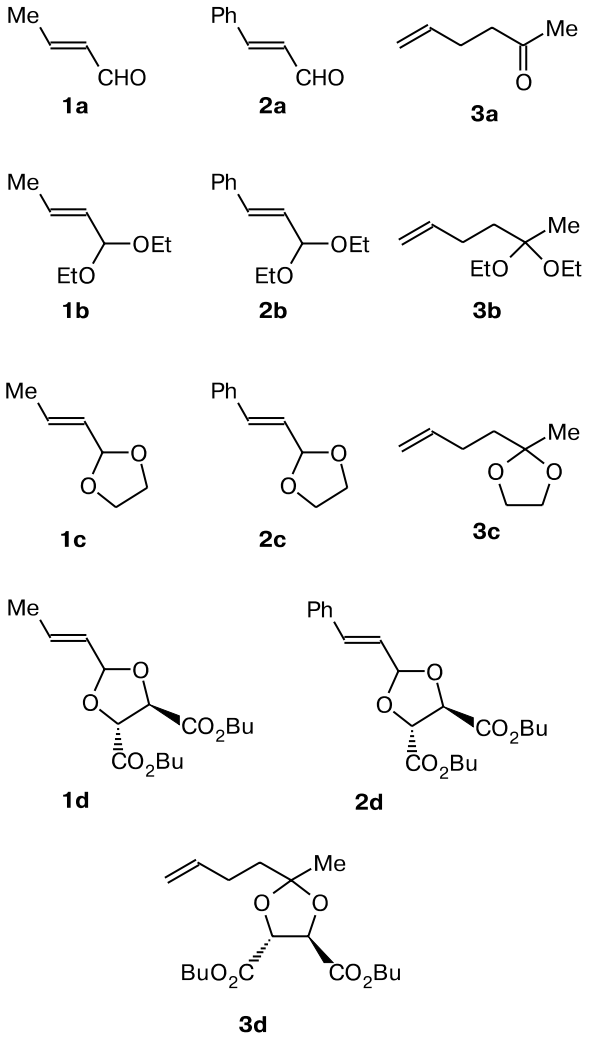
Cyclopropanation was carried out at 5—10 °C by adding a solution of CH_2N_2 in Et_2O or CH_2Cl_2 to an unsaturated compound in the presence of a catalyst in the olefin : CH_2N_2 : catalyst molar ratio of 1 : 3 : 0.02 for 30 min. Investigation of cyclopropanation of dioxolane **2c** with the use of $Pd(OAc)_2$, $PdCl_2$, $Pd(acac)_2$, CuCl, $[CuOTf]_2 \cdot C_6H_6$, $Cu(acac)_2$, and $Cu(OTf)_2$, as the catalysts demonstrated that $Pd(acac)_2$ and $Cu(OTf)_2$ are the most efficient palladium and copper catalysts, respectively, under the reaction conditions used. Cyclopropanation catalyzed by $Pd(acac)_2$ or $Cu(OTf)_2$ afforded products in 99 and 49% yields, respectively. Hence, all further reactions were carried out with the use of these two catalysts.

Study of the influence of the nature of the starting reagents on the reaction pathway showed that both the structures of unsaturated carbonyl compounds **1a—c** and the catalyst have a substantial effect. The reactions of conjugated aldehydes **1a** and **2a** with CH_2N_2 in the presence of $Pd(acac)_2$ afford the corresponding cyclopropanecarbaldehydes **4** and **5** (Scheme 1) in moderate yields (35 and 60%, respectively). In the reaction with

* For Part 14, see Ref. 1.

** Dedicated to Corresponding Member of the Russian Academy of Sciences E. P. Serebryakov on the occasion of his 70th birthday.

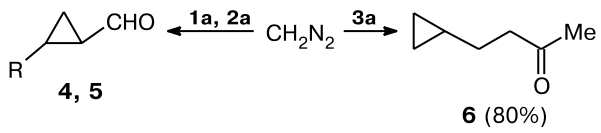
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 979—983, April, 2005.



hexenone **3a**, cyclopropanation of the C=C bonds occurs more efficiently, and, in the presence of $Pd(acac)_2$, 4-cyclopropylbutan-2-one (**6**) is produced in 80% yield. The relatively high yield of cyclopropane **6** is consistent with the facts that palladium catalysts are very sensitive to the steric effects of the substrate and the reactions with their use result in efficient cyclopropanation predominantly of monosubstituted and strained endocyclic double bonds.[3] In turn, the observed moderate yields of cyclopropane-containing aldehydes **4** and **5** are partially associated with the competitive 1,3-dipolar cycloaddition of diazomethane to conjugated aldehydes **1a** and **2a** (in the case of cinnamaldehyde **2a**, *trans*-4-phenyl-1-pyrazoline-3-carbaldehyde[7] was isolated in 37% yield).

In the reaction with the use of $Cu(OTf)_2$ as the catalyst, cinnamaldehyde **2a** undergoes cyclopropanation by only 10%. The reaction of crotonaldehyde with diazomethane proceeds by another mechanism to give *trans*-2,4-diprop-1-enyl-1,3-dioxolane (**7**) as the major product in ~30% yield (Scheme 2). Apparently, in the initial step of the reaction giving rise to this compound,

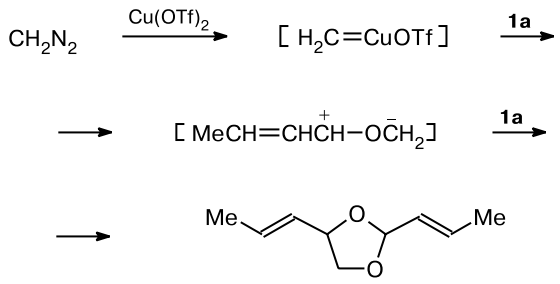
Scheme 1



R = Me (**4**), Ph (**5**)

the methylene complex [CH_2=CuOTf] interacts with the carbonyl group of crotonaldehyde rather than with the C=C bond. The resulting unstable *O*-ylide adds as the 1,3-dipole at the C=O bond of the second aldehyde molecule.[12]

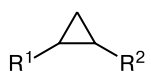
Scheme 2



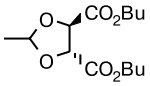
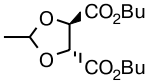
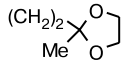
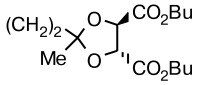
Crotonaldehyde derivatives **1b,c** react with CH_2N_2 in the presence of $Pd(acac)_2$ or $Cu(OTf)_2$ to give a complex mixture of products. By contrast, cyclic acetal **1d** containing two electron-withdrawing butoxycarbonyl groups at positions 4 and 5 of the dioxolane fragment is readily subjected to cycloprotonation in the presence of $Pd(acac)_2$ to form dibutyl 2-(*trans*-2-methylcyclopropyl)-1,3-dioxolane-*trans*-4,5-dicarboxylate (**8**) (Table 1). Unlike simple crotonaldehyde derivatives **1b,c**, cinnamaldehyde derivatives **2b—d** react with CH_2N_2 in the presence of $Pd(acac)_2$ to give the corresponding cyclopropane derivatives **9—11** in high yields. Cyclopropanation of hexenone derivatives **3b—d** occurs with a somewhat higher efficiency compared to ketone **3a** and produces cyclopropanes **12—14** in 87—99% yields (see Table 1).

The $Cu(OTf)_2$ catalyst is less efficient than $Pd(acac)_2$ in cyclopropanation of cinnamaldehyde derivatives **2b—d** or hexenone derivatives **3b—d**, and these reactions give the corresponding cyclopropanes in low yields (see Table 1). In the reactions of unsaturated compounds **2b** and **2d**, $Cu(OTf)_2$ catalyzes the acetal deprotection giving rise to the starting cinnamaldehyde **2a**, the reaction being typical only of cinammaldehyde derivatives. Special studies showed that cyclopropane derivatives **9—14** are not transformed into the corresponding carbonyl compounds under the action of $Cu(OTf)_2$.

Table 1. Yields of products **8—14** of catalytic cyclopropanation of unsaturated acetals and ketals in the presence of $Pd(acac)_2$ or $Cu(OTf)_2$



8—14

Compound	R^1	R^2	Product	Yield (%)	
				$Pd(acac)_2$	$Cu(OTf)_2$
1d	Me		**8**	95	10
2b	Ph	$CH(OEt)_2$	**9**	98	12 + **2a** (37)
2c	Ph		**10**	98	49
2d	Ph		**11**	99	**2a** (60)
3b	H	$(CH_2)_2$—$CMe(OEt)_2$	**12**	92	60
3c	H		**13**	87	75
3d	H		**14**	99	80

The resulting cyclopropanes were isolated by preparative TLC and characterized by ^1H and ^{13}C NMR spectroscopy. In some cases, the assignment of the signals of the H and C atoms was made using the {C,H}-correlation techniques. Studies of the reactions of cyclic acetals **8** and **11** showed that the acetal deprotection with TsOH occurs rather successfully to give cyclopropane-containing aldehydes **4** and **5** in 68 and 79% yields, respectively.

Higher efficiency of Pd compounds in cyclopropanation of unsaturated carbonyl compounds and their acetals compared to Cu compounds is, apparently, associated with the difference in the mechanism of their action. It is believed (see the study[3] and references cited therein) that the generation of a carbene complex, *i.e.*, the reaction of CH_2N_2 with the catalyst, is an important step in reactions performed in the presence of copper catalysts. By contrast, the formation of a π-olefin complex with a catalyst, in particular, with low-valent Pd, plays a considerable role in reactions with the use of palladium catalysts. In the former case, the efficiency of the target cyclopropanation reaction is determined not only by the nature of the C=C bond but also by the fact that the side reaction of the carbene complex with the next CH_2N_2 molecule proceeds easily. In the latter case, the efficiency of the target reaction depends on stability of the π-olefin complex, which can react with the CH_2N_2 molecule. This is quite suitable for cyclopropanation of crotonaldehyde and cinnamaldehyde. However, in reactions with these unsaturated compounds, the competitive 1,3-dipolar cycloaddition of CH_2N_2 to the C=C bond plays a noticeable role. Cyclopropanation of acetal derivatives is, on the whole, favorable and gives the corresponding cyclopropanes in high yields due, apparently, to intramolecular stabilization of π-olefin complexes by oxygen atoms.

To summarize, the study of catalytic cyclopropanation of 1,2-disubstituted double bonds in unsaturated carbonyl compounds and their acetal (ketal) derivatives with diazomethane provided evidence for higher selectivity of cyclopropanation of the latter compared to the starting unsaturated carbonyl compounds and for the activating effect of the acetal fragments on the reactivity of the C=C bond compared to cyclopropanation of usual 1,2-disubstituted alkenes.[3] Palladium compounds, in particular, $Pd(acac)_2$, are catalysts of choice for cyclopropanation of acetal derivatives of unsaturated carbonyl compounds.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz, respectively) in $CDCl_3$ with $SiMe_4$ as the internal standard. The IR spectra were measured on a Specord M82-63 instrument in a thin layer. The GLC analysis was carried out on a Chrom-5 chromatograph equipped with a flame ionization detector (a 1200×5 mm column with 5% SE-30 on Inerton N-AW DMCS (0.125—0.160 mm)) using helium as the carrier gas. The TLC analysis was carried out on Silufol chromatographic plates (Merck). Preparative separation was performed by column chromatography on silica gel 60 (0.040—0.063 mm). Cinnamaldehyde **2a**,[13] diethylacetals **1b—3b**,[14] and 1,3-dioxolanes **1c—3c** and **1d—3d**[7,15] were synthesized according to known procedures. Crotonaldehyde (**1a**) and hex-5-en-2-one (**3a**) were distilled under a stream of argon and stored over hydroquinone. The solvents (Et_2O, CH_2Cl_2, benzene, hexane, petroleum ether, THF, and AcOEt) were purified according to standard procedures.[16]

2-*trans*-Prop-1-enyl-1,3-dioxolane (1c). The yield was 30%, colorless liquid, b.p. 34 °C (7 Torr). Found (%): C, 63.10; H, 8.74. $C_6H_{10}O_2$. Calculated (%): C, 63.14; H, 8.83. IR, ν/cm^{-1}: 760, 832, 964, 1054, 1120, 1216, 1396, 1462, 1510, 1540, 1678, 2890. ^1H NMR, δ: 1.46 (d, 3 H, Me, ^3J = 6.3 Hz); 3.52—3.80 (m, 4 H, $H_2C(4)$ and $H_2C(5)$); 4.87 (d, 1 H, H(2), ^3J = 6.3 Hz); 5.23 (dd, 1 H, H(1′), ^3J = 6.3 Hz, ^3J = 13.7 Hz); 5.67 (dq, 1 H, H(2′), ^3J = 6.8 Hz, ^3J = 13.7 Hz). ^{13}C NMR, δ: 16.9 (Me); 64.4 (C(4) and C(5)); 103.6 (C(2)); 127.1 (C(2′)); 132.3 (C(1′)).

Dibutyl 2-(*trans*-prop-1-enyl)-1,3-dioxolane-*trans*-4,5-dicarboxylate (1d). The yield was 33%, the compound was isolated by column chromatography, R_f 0.86 (petroleum ether—AcOEt, 7 : 3, as the eluent). Found (%): C, 61.08; H, 8.36. $C_{16}H_{26}O_6$. Calculated (%): C, 61.13; H, 8.34. IR, ν/cm^{-1}: 604, 688, 742, 832, 964, 1012, 1090, 1192, 1378, 1456, 1510, 1690, 1744, 2872, 2962. ^1H NMR, δ: 0.95 (t, 6 H, 2 Me, ^3J = 7.3 Hz); 1.40 (sextet, 4 H, 2 CH_2, ^3J = 7.3 Hz); 1.63—1.73 (m, 4 H, 2 CH_2); 1.76 (d, 3 H, Me, ^3J = 6.3 Hz); 4.21—4.32 (m, 4 H, 2 OCH_2); 4.71 and 4.79 (both d, 1 H each, H(4), H(5), ^3J = 3.7 Hz); 5.51 (d, 1 H, H(2), ^3J = 4.3 Hz); 5.61 (dd, 1 H, H(1′), ^3J = 12.1 Hz, ^3J = 4.3 Hz); 6.01—6.09 (dq, 1 H, H(2′), ^3J = 6.3 Hz, ^3J = 12.1 Hz). ^{13}C NMR, δ: 13.6 (2 Me); 17.6 (Me); 19.0 and 30.5 (2 CH_2 each); 65.8 (2 OCH_2); 72.0 and 77.3 (C(4) and C(5)); 100.7 (C(2)); 126.6 (C(1′)); 134.9 (C(2′)); 171.6 (2 COO).

Dibutyl 2-(*trans*-2-phenylvinyl)-1,3-dioxolane-*trans*-4,5-dicarboxylate (2d). The yield was 70%, yellow oil, was isolated by column chromatography, R_f 0.77 (petroleum ether—AcOEt, 7 : 3, as the eluent). Found (%): C, 67.08; H, 7.33. $C_{21}H_{28}O_6$. Calculated (%): C, 67.75; H, 7.37. IR, ν/cm^{-1}: 694, 754, 964, 1090, 1144, 1210, 1576, 1624, 1678, 1744, 2872, 2932, 2956. ^{1}H NMR, δ: 0.82—0.97 (m, 6 H, 2 Me); 1.33—1.45, 1.34—1.47, and 4.17—4.29 (all m, 4 H each, 3 CH_2); 4.77 and 4.87 (both d, 1 H each, H(4) and H(5), ^3J = 3.7 Hz); 5.81 (d, 1 H, H(2), ^3J = 6.7 Hz); 6.26 (dd, 1 H, H(1′), ^3J = 16.0 Hz, ^3J = 6.7 Hz); 6.84 (d, 1 H, H(2′), ^3J = 16.0 Hz); 7.19—7.29 (m, 5 H, Ar). ^{13}C NMR, δ: 13.4 (2 Me); 18.9 and 30.3 (2 CH_2 each); 65.9 (2 OCH_2); 72.0 and 77.3 (C(4) and C(5)); 107.0 (C(2)); 123.6 (C(1′)); 135.3 (C(2′)); 125.7—128.1 (5 CH, Ar); 135.3 (C, Ar); 169.5 (COO).

5,5-Diethoxyhex-1-ene (3b). The yield was 35%, colorless liquid, b.p. 70 °C (40 Torr). Found (%): C, 69.65; H, 11.74. $C_{10}H_{20}O_2$. Calculated (%): C, 69.72; H, 11.70. IR, ν/cm^{-1}: 850, 916, 1054, 1126, 1216, 1252, 1372, 1642, 2974. ^{1}H NMR, δ: 1.17 and 1.23 (both t, 3 H each, Me, ^3J = 7.1 Hz); 1.30 (s, 3 H, Me); 1.71—1.74 (m, 2 H, $H_2C(4)$); 2.06—2.12 (m, 2 H, $H_2C(3)$); 3.45 and 3.71 (both q, 2 H each, CH_2, ^3J = 7.1 Hz); 4.95 (dd, 1 H, *trans*-HC(1), ^2J = 1.6 Hz, $^3J_{cis}$ = 10.4 Hz); 5.25 (dd, 1 H, *cis*-HC(1), ^2J = 1.6 Hz, $^3J_{trans}$ = 17.0 Hz); 5.83 (ddt, 1 H, HC=, ^3J = 6.4 Hz, ^3J = 10.4 Hz, ^3J = 17.0 Hz). ^{13}C NMR, δ: 15.4, 18.2, and 22.0 (all Me); 28.6 (C(3)); 36.4 (C(4)); 55.5 (2 OCH_2); 101.3 (C(5)); 114.2 (C(1)); 138.4 (C(2)).

2-(But-3-enyl)-2-methyl-1,3-dioxolane (3c). The yield was 34%, colorless liquid, b.p. 50 °C (20 Torr). Found (%): C, 67.67; H, 9.86. $C_8H_{14}O_2$. Calculated (%): C, 67.57; H, 9.92. IR, ν/cm^{-1}: 520, 628, 1054, 1126, 1372, 1450, 1642, 1720, 2878, 2944, 2980. ^{1}H NMR, δ: 1.31 (s, 3 H, Me); 1.69—1.74 (m, 2 H, $H_2C(1′)$); 2.07—2.18 (m, 2 H, $H_2C(2′)$); 3.89—3.95 (m, 4 H, $H_2C(4)$ and $H_2C(5)$); 4.91 (dd, 1 H, *trans*-HC(1), ^2J = 1.8 Hz, $^3J_{cis}$ = 10.2 Hz); 5.00 (dd, 1 H, *cis*-HC(1), ^2J = 1.6 Hz, $^3J_{trans}$ = 17.2 Hz); 5.82 (ddt, 1 H, =CH, ^3J = 6.5 Hz, ^3J = 10.2 Hz, ^3J = 17.2 Hz). ^{13}C NMR, δ: 23.7 (Me); 28.2 (C(2′)); 38.1 (C(3′)); 64.5 (C(4) and C(5)); 109.6 (C(2)); 114.1 (=CH_2); 138.4 (=CH).

Dibutyl 2-(but-3-enyl)-2-methyl-1,3-dioxolane-*trans*-4,5-dicarboxylate (3d). The yield was 30%, yellow liquid, b.p. 140 °C (1 Torr). Found (%): C, 63.22; H, 8.89. $C_{18}H_{30}O_6$. Calculated (%): C, 63.14; H, 8.83. ^{1}H NMR, δ: 0.96 (t, 6 H, 2 Me, ^3J = 6.2 Hz); 1.35—1.46 (m, 4 H, 2 CH_2); 1.48 (s, 3 H, Me); 1.63—1.74 (m, 4 H, 2 CH_2); 1.83—1.89 (m, 2 H, CH_2); 2.21—2.26 (m, 2 H, =CHC$\underline{H}_2$); 4.21—4.33 (m, 4 H, 2 OCH_2); 4.71 and 4.80 (both d, 1 H each, H(4) and H(5), ^3J = 6.2 Hz); 4.95 (dd, 1 H, *trans*-HC(1), ^2J = 1.6 Hz, $^3J_{cis}$ = 10.3 Hz); 5.03 (dd, 1 H, *cis*-HC(1), ^2J = 1.6 Hz, $^3J_{trans}$ = 17.0 Hz); 5.83 (ddt, 1 H, =CH, ^3J = 6.5 Hz, ^3J = 10.3 Hz, ^3J = 17.0 Hz). ^{13}C NMR, δ: 13.5 (2 Me); 17.5 (Me); 18.9 (2 $\underline{C}H_2$Me); 30.4 (2 CH_2); 65.1 (2 OCH_2); 72.0 and 76.6 (C(4) and C(5)); 107.3 (C(2)); 116.0 (=CH_2); 134.8 (=CH); 171.5 (COO).

Cyclopropanation of unsaturated carbonyl compounds and their derivatives (general procedure). A 0.45—0.47 *M* CH_2N_2 solution in Et_2O (45 mL, ~21 mmol) was added with stirring to a solution of a carbonyl compound or its derivative (7.0 mmol) and $Pd(acac)_2$ (0.042 g, 0.14 mmol) in Et_2O (20 mL) (or $Cu(OTf)_2$ (0.051 g, 0.14 mmol) in CH_2Cl_2 (20 mL)) at 5—10 °C for 30 min. The reaction mixture was additionally stirred for 30—40 min and passed through a thin layer of Al_2O_3. The solvent was removed in low vacuum. The residue was distilled or chromatographed on SiO_2. The yields of the reaction products are given in Table 1. The physicochemical and spectroscopic characteristics of compounds **4**,[17] **5**,[7] **7**,[12] and **10**[15] are consistent with the published data.

4-Cyclopropylbutan-2-one (6). The product was isolated by column chromatography, R_f 0.83 (petroleum ether—AcOEt, 20 : 1, as the eluent). Found (%): C, 74.90; H, 10.78. $C_7H_{12}O$. Calculated (%): C, 74.95; H, 10.83. IR, ν/cm^{-1}: 820, 910, 1126, 1258, 1378, 1456, 1672, 2854, 2926, 3076. ^{1}H NMR, δ: –0.06 and 0.30 (both m, 2 H each, CH_2CH_2); 0.56 (m, 1 H, CH); 1.35 (q, 2 H, $H_2C(4)$, ^3J = 7.2 Hz); 2.04 (s, 3 H, Me); 2.43 (t, 2 H, $H_2C(3)$, ^3J = 7.2 Hz). ^{13}C NMR, δ: 4.5 (CH_2CH_2); 10.6 (CH); 29.0 (C(4)); 30.0 (C(1)); 43.8 (C(3)); 209.3 (C(2)).

Dibutyl 2-(*trans*-2-methylcyclopropyl)-1,3-dioxolane-*trans*-4,5-dicarboxylate (8). The product was isolated by column chromatography, R_f 0.80 (petroleum ether—AcOEt, 7 : 3, as the eluent). Found (%): C, 62.12; H, 8.54. $C_{17}H_{28}O_6$. Calculated (%): C, 62.18; H, 8.59. Compound **8** was prepared as a mixture of two diastereomers in a ratio of 1 : 5 or 1 : 1.2 with the use of $Pd(acac)_2$ or $Cu(OTf)_2$, respectively. The diastereomers are characterized by slightly different positions of the signals in the ^{13}C NMR spectra. ^{1}H NMR, δ: 0.36—0.42 and 0.62—0.70 (both m, 1 H each) and 0.81—0.90 (m, 2 H, protons of the cyclopropane ring); 0.92 (t, 3 H, Me, ^3J = 7.3 Hz); 1.05 (d, 3 H, Me, ^3J = 5.6 Hz); 1.38 (sextet, 4 H, 2 C$\underline{H}_2$Me, ^3J = 7.3 Hz); 1.59—1.70 (m, 4 H, 2 CH_2); 4.19 (q, 4 H, 2 OCH_2, ^3J = 6.6 Hz); 4.61 (d, 1 H, H(5), ^3J = 4.0 Hz); 4.71—4.76 (m, 2 H, H(4) and H(2)).

Minor diastereomer (**8a**). ^{13}C NMR, δ: 9.4 (HC(2′)); 9.6 ($H_2C(3′)$); 13.4 and 17.7 (both Me); 18.8 ($\underline{C}H_2$Me); 20.9 (HC(1′)); 30.3 (CH_2); 65.4 (OCH_2); 76.4 (HC(4), HC(5)); 110.4 (HC(2)); 169.7 (COO).

Major diastereomer (**8b**). ^{13}C NMR, δ: 9.4 (HC(2′)); 9.6 ($H_2C(3′)$); 13.4 and 17.8 (both Me); 18.8 ($\underline{C}H_2$Me); 21.0 (HC(1′)); 30.3 (CH_2); 65.5 (OCH_2); 76.7 (HC(4), HC(5)); 110.6 (HC(2)); 169.1 (COO).

***trans*-2-(Diethoxymethyl)-1-phenylcyclopropane (9).** The product was isolated by column chromatography, R_f 0.77 (petroleum ether—AcOEt, 20 : 1, as the eluent). Found (%): C, 76.30; H, 9.21. $C_{14}H_{20}O_2$. Calculated (%): C, 76.33; H, 9.15. IR, ν/cm^{-1}: 700, 754, 1060, 1120, 1372, 1444, 1498, 1606, 1654, 2926, 2974. ^{1}H NMR, δ: 0.91—1.03 (m, 2 H); 1.08—1.14 and 1.41—1.48 (both m, 1 H each, protons of the cyclopropane ring); 1.21 and 1.23 (both t, 6 H, 2 Me, ^3J = 6.8 Hz); 3.44—3.73 (m, 4 H, 2 OCH_2); 4.43 (d, 1 H, C$\underline{H}(OEt)_2$, ^3J = 4.8 Hz); 7.07—7.28 (m, 5 H, Ar). ^{13}C NMR, δ: 12.4 (CH_2); 15.3 (Me); 19.4 and 25.4 (2 CH of the cyclopropane ring); 60.8 and 61.2 (2 OCH_2); 102.7 ($\underline{C}H(OEt)_2$); 125.5—128.6 (5 CH, Ar); 142.4 (C, Ar).

Dibutyl 2-(2-*trans*-phenylcyclopropyl)-1,3-dioxolane-*trans*-4,5-dicarboxylate (11). Yellow liquid, b.p. 209 °C (0.1 Torr). Found (%): C, 67.78; H, 7.78. $C_{22}H_{30}O_6$. Calculated (%): C, 67.70; H, 7.74. IR, ν/cm^{-1}: 694, 754, 964, 1090, 1144, 1210, 1576, 1624, 1678, 1744, 2872, 2932, 2956. Compound **11** was prepared as a mixture of two diastereomers in a ratio of 1 : 10 with the use of $Pd(acac)_2$, The diastereomers are characterized by slightly different positions of the signals in the NMR spectra. ^{1}H NMR, δ: 1.08 (t, 3 H, Me, ^3J = 7.3 Hz); 1.10 (t, 3 H, Me, ^3J = 7.2 Hz); 1.19 and 1.37 (both m, 1 H each, $H_2C(3′)$); 1.54 (sextet, 4 H, 2 C$\underline{H}_2$Me, ^3J = 7.3 Hz); 1.74—1.84 (m, 4 H, 2 CH_2); 2.24—2.34 (m, 2 H, HC(1′) and HC(2′)); 4.33—4.39

(m, 4 H, 2 OCH_2); 4.84 (d, 1 H, H(4), ^3J = 3.8 Hz); 4.95 (d, 1 H, H(5), ^3J = 3.9 Hz); 5.23 (minor diastereomer) and 5.26 (major diastereomer) (both d, 1 H, H(2), ^3J = 6.0 Hz); 7.24—7.43 (m, 5 H, Ar).

Minor diastereomer (**11a**). ^{13}C NMR, δ: 10.8 (Me); 11.5 (C(3′)); 13.5 and 23.8 (C(1′) and C(2′)); 18.8 ($\underline{C}H_2Me$); 19.4 (Me); 30.3 (CH_2); 65.6 (OCH_2); 77.2 (C(4) and C(5)); 108.8 (C(2)); 125.7—128.1 (5 CH, Ar); 141.2 (C, Ar); 169.1 (COO).

Major diastereomer (**11b**). ^{13}C NMR, δ: 10.8 (Me); 11.7 (C(3′)); 13.5 and 24.0 (C(1′) and C(2′)); 18.8 ($C\underline{H}_2Me$); 19.4 (Me); 30.3 (CH_2); 65.6 (OCH_2); 76.8 (C(4) and C(5)); 109.3 (C(2)); 125.7—128.1 (5 CH, Ar); 141.1 (C, Ar); 169.6 (COO).

4-Cyclopropyl-2,2-diethoxybutane (12). The product was isolated by column chromatography, R_f 0.57 (petroleum ether—AcOEt, 20 : 1, as the eluent). Found (%): C, 70.97; H, 11.86. $C_{11}H_{22}O_2$. Calculated (%): C, 70.92; H, 11.90. IR, ν/cm^{-1}: 814, 850, 952, 1012, 1054, 1114, 1222, 1258, 1372, 1456, 2854, 2926, 3070. ^{1}H NMR, δ: 0.02 and 0.39 (both m, 2 H each, CH_2CH_2 in the cyclopropane ring, ^2J = 5.6 Hz, $^3J_{trans}$ = 4.8 Hz, $^3J_{cis}$ = 8.0 Hz); 0.65 (m, 1 H, CH); 0.89 (q, 2 H, $H_2C(4)$, ^3J = 7.3 Hz); 1.22 (t, 6 H, 2 Me, ^3J = 7.1 Hz); 1.26 (s, 3 H, Me); 1.69—1.78 (m, 2 H, $H_2C(3)$); 3.38—3.52 (q, 4 H, 2 OCH_2, ^3J = 7.1 Hz). ^{13}C NMR, δ: 4.4 (CH_2CH_2 in the cyclopropane ring); 11.0 (CH); 15.4 (Me); 28.5 (C(4)); 29.5 (C(1)); 36.5 (C(3)); 55.4 (OCH_2); 101.2 (C(2)).

2-(2-Cyclopropylethyl)-2-methyl-1,3-dioxolane (13). The product was isolated by column chromatography, R_f 0.63 (petroleum ether—AcOEt, 20 : 1, as the eluent). Found (%): C, 69.24; H, 10.66. $C_9H_{16}O_2$. Calculated (%): C, 69.19; H, 10.32. IR, ν/cm^{-1}: 466, 814, 862, 946, 1018, 1072, 1222, 1258, 1378, 1462, 1522, 1714, 2926, 3076. ^{1}H NMR, δ: –0.12 and 0.34 (both m, 2 H each, CH_2CH_2 in the cyclopropane ring); 0.57 (m, 1 H, CH); 1.08—1.18 (m, 2 H, $C\underline{H}_2CH$); 1.22 (s, 3 H, Me); 1.62—1.70 (m, 2 H, CH_2C); 3.79—3.86 (m, 4 H, $H_2C(4)$ and $H_2C(5)$). ^{13}C NMR, δ: 4.5 and 4.9 (CH_2CH_2 in the cyclopropane ring); 15.3 (CH); 25.5 (Me); 28.5 ($\underline{C}H_2CH$); 36.5 ($\underline{C}H_2C$); 64.6 (C(4) and C(5)); 101.6 (C(2)).

Dibutyl 2-(2-cyclopropylethyl)-2-methyl-1,3-dioxolane-*trans*-4,5-dicarboxylate (14). The product was isolated by column chromatography, R_f 0.84 (petroleum ether—AcOEt, 7 : 3, as the eluent). Found (%): C, 64.09; H, 9.08. $C_{19}H_{32}O_6$. Calculated (%): C, 64.02; H, 9.05. IR, ν/cm^{-1}: 700, 742, 1102, 1204, 1372, 1456, 1732, 2356, 2866, 2926, 2956. ^{1}H NMR, δ: –0.03 and 0.35 (both m, 2 H each, CH_2CH_2 in the cyclopropane ring); 0.61 (m, 1 H, CH); 0.91 (t, 6 H, 2 Me, ^3J = 7.3 Hz); 1.35—1.46 (m, 4 H, 2 CH_2); 1.39 (s, 3 H, Me); 1.51 (q, 2 H, CH_2CH, ^3J = 8.1 Hz); 1.63—1.74 (m, 4 H, 2 CH_2); 1.83 (t, 2 H, CH_2C, ^3J = 8.1 Hz); 4.19 (t, 4 H, 2 OCH_2, ^3J = 6.7 Hz); 4.64—4.72 (m, 2 H, HC(4) and HC(5)). ^{13}C NMR, δ: 4.4 and 4.5 (CH_2CH_2 in the cyclopropane ring); 12.6 (CH); 13.6 ($CH_2\underline{Me}$); 19.0 ($\underline{C}H_2Me$); 24.5 (Me); 29.7 ($\underline{C}H_2CH$); 30.5 (CH_2); 39.2 ($\underline{C}H_2C$); 65.6 (2 OCH_2); 77.3 (C(4) and C(5)); 115.3 (C(2)); 169.8 (COO).

***trans*-2-Methylcyclopropanecarbaldehyde (4).** A solution of acetal **8** (1.20 g, 3.7 mmol) and TsOH (0.22 g) in MeOH (12 mL) was stirred at 25 °C for 48 h. The reaction mixture was filtered, treated with solid $NaHCO_3$, and extracted with pentane (2×10 mL). The organic layer was dried with anhydrous Na_2SO_4 and distilled. The fraction with b.p. 65—67 °C was collected. Aldehyde **4** was obtained in a yield of 0.21 g (68%).

***trans*-2-Phenylcyclopropanecarbaldehyde (5).** A solution of acetal **11** (1.67 g, 4.3 mmol) and TsOH (1.0 g) in a mixture of THF (50 mL) and water (10 mL) was refluxed for 25 h. Then the reaction mixture was filtered, treated with solid $NaHCO_3$, and extracted with pentane (2×10 mL). The organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. Column chromatography afforded aldehyde **5**, R_f 0.75 (petroleum ether—AcOEt, 7 : 3, as the eluent), in a yield of 0.50 g (79%).

This study was financially supported by the Chemistry and Materials Science Division of the Russian Academy of Sciences (Program "Theoretical and Experimental Studies of the Nature of Chemical Bonds and Mechanisms of Important Chemical Reactions and Processes").

References

1. Yu. V. Tomilov, E. V. Guseva, N. V. Volchkov, and E. V. Shulishov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2019 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2113].
2. H. Lebel, J.-F. Marcoux, C. Molinaro, and A. B. Charette, *Chem. Rev.*, 2003, **103**, 977.
3. Yu. V. Tomilov, V. A. Dokichev, U. M. Dzhemilev, and O. M. Nefedov, *Usp. Khim.*, 1993, **62**, 847 [*Russ. Chem. Rev.*, 1993, **62**, 799 (Engl. Transl.)].
4. O. M. Nefedov, A. I. Ioffe, and L. G. Menchikov, *Khimiya karbenov* [*Carbene Chemistry*], Khimiya, Moscow, 1990, p. 158 (in Russian).
5. I. E. Dolgy, E. A. Shapiro, and O. M. Nefedov, *Chemistry of Carbenes and Small-Sized Cyclic Compounds*, Ed. O. M. Nefedov, Mir, Moscow, 1989, p. 101.
6. L. A. Yanovskaya, V. A. Dombrovskii, and A. Kh. Khusid, *Tsiklopropany s funktsional´nymi gruppami* [*Cyclopropanes with Functional Groups*], Nauka, Moscow, 1980, 224 pp. (in Russian).
7. I. Arai, A. Mori, and H. Yamamoto, *J. Am. Chem. Soc.*, 1985, **107**, 8254.
8. Patent US 2005/0042242A1 [*Citral Derivatives*].
9. H. Abdallah, R. Grée, and R. Carrié, *Tetrahedron Lett.*, 1982, **23**, 503.
10. J. E. A. Luithle and J. Pietruszka, *Eur. J. Org. Chem.*, 2000, 2557.
11. R. M. Sultanova, V. R. Katashova, D. A. Petrov, A. A. Fatykhov, S. S. Zlotskii, and V. A. Dokichev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 828 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 865].
12. Y. Noichi, *Nippon Kagaku Zasshi*, 1967, **88**, 565; *Chem. Abstr.*, 1968, **69**, 10389x.
13. C. J. Schmiddle and P. G. Barnett, *J. Am. Chem. Soc.*, 1956, **78**, 3210.
14. V. V. Mezheritskii, E. P. Olekhnovich, S. M. Luk´yanov, and G. N. Dorofeenko, *Ortoefiry v organicheskom sinteze* [*Orthoesters in Organic Synthesis*], Izd-vo Rostovskogo Un-ta, Rostov, 1976, 176 pp. (in Russian).
15. S. E. Denmark and J. P. Edwards, *J. Org. Chem.*, 1991, **56**, 6974.
16. F. J. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley, New York—London—Sidney—Toronto, 1972.
17. J.-L. Ripoll and J.-M. Conia, *Bull. Soc. Chim. Fr.*, 1965, **10**, 2755.

Received February 8, 2005