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EFFECT OF THE IMIDAZOLIUM SALTS ON THE CATALYTIC INTERACTION OF METHYL DIAZOACETATE WITH CINNAMALDEHYDE ETHYLENE ACETAL IN THE PRESENCE OF Cu- AND Rh- CONTAINING CATALYSTS

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Interaction of cinnamaldehyde ethylene acetal with methyl diazoacetate, catalyzed by $Rh_2(OAc)_4$ and $Cu(OTf)_2$, in the presence of the $[bmim]^+Cl^-$, $[bmim]^+BF_4^-$, $[bmim]^+PF_6^-$ has been studied. It was shown that addition of the imidazolium salts effects on regioselectivity of the reaction and enables to obtain methyl ester of 2-(1,3-dioxolane-2-yl)-3-phenyl-cyclopropanecarboxylic acid with moderate yield.

INTRODUCTION

In recent years, much attention has been focused on developing new regio- and stereoselective methods for the preparation of 1,4-diheterocycloalkanes. First of all, this is due to high various physiological activities of these heterocyclic compounds. For example, a morpholine fragment - one of the most common elements of the structure of pharmaceutical products [1] and tagetitoksin containing of 1,4-oxathiane fragment is an inhibitor of RNA polymerase.[2] Intramolecular rearrangement of oxonium, ammonium and sulfonium ylides, formed by the catalytic interaction of diazo compounds with 1,3-diheterocycloalkanes, is one of convenient methods for the synthesis of 1,4-dioxane, morpholine and 1,4-oxathiane derivatives. Earlier we studied the interaction of mono-, di- and three substituted 1,3-dioxolane with methyl diazoacetate in the presence of $BF_3{\cdot}OEt_2$, $Cu(OTf)_2$, $CuCl_2$, $CuSO_4$, $Rh_2(CF_3CO_2)_4$, $Rh(PPh_3)_3Cl$, $Rh_2(OAc)_4$, $Ru_2(OAc)_4Cl$, including use of imidazolium salts ($[bmim]^+Cl^-$, $[bmim]^+BF_4^-$, $[bmim]^+PF_6^-$).[8-13] This kind of conversion goes on the through intermediate formation of ylides that seems easy. If the molecule contains the other reaction centers, the reaction of C-X insertion competes with reactions X-H (X = C, O, S, N) insertion, cyclopropanation and other catalytic processes.[14]

In this connection, research of ethylene ketals/acetals α,β-unsaturated carbonyl compounds with diazocarbonyl compounds in catalytic reactions is interesting.

RESULTS AND DISCUSSION

Previously we found that 1,4-dioxa- and 1,4-oxathiolanes are formed when methyl diazoacetate reacts with 2-(alke-1-nyl)-1,3-dioxa- and 1,3-oxathiolanes in presence $Rh_2(OAc)_4$, moreover

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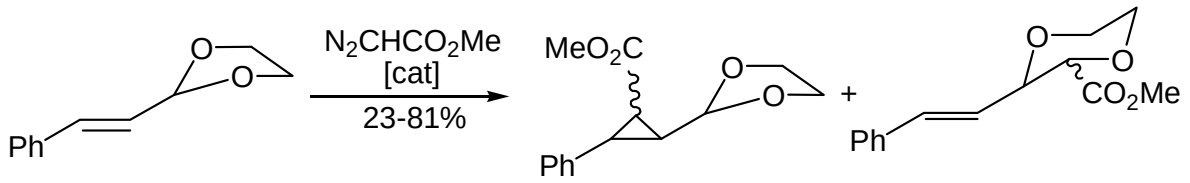
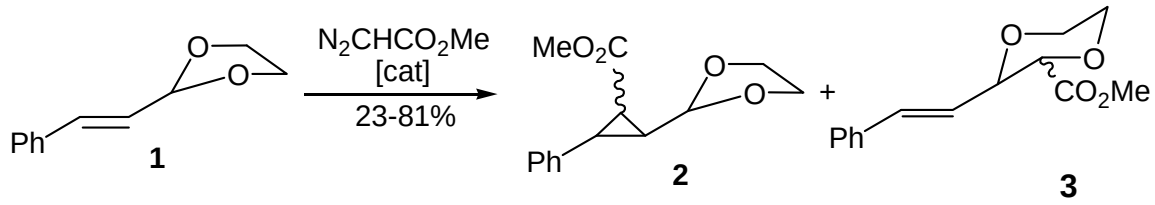
2,3,5,6-tetrahydro-1,4-dioxa- and 2,3,5,6-tetrahydro-1,4-oxytocines are formed as a result of [2,3]-sigmatropic rearrangement of intermediately formed oxonium and sulfonium ylides. The products formation by cycloaddition of methoxycarbonyl carbene to the C=C bond is not observed.[15]

In this study we investigated the catalytic interaction of methyl diazoacetate with 2[(*E*)-2-phenylvinyl]-1,3-dioxolane **1** in the presence of $Rh_2(OAc)_4$ or $Cu(OTf)_2$ and imidazolium salts – $[bmim]^+Cl^-$, $[bmim]^+BF_4^-$, $[bmim]^+PF_6^-$. The experiments have been conducted by adding methyl diazoacetate to a solution of **1** compounds in CH_2Cl_2 or $ClCH_2CH_2Cl$ (the molar ratio olefin - N_2CHCO_2Me - catalyst 1:1:0.01).

Experiments showed (Table 1) that the products of [2+1] addition – methyl ester of 2-(1,3-dioxolane-1-yl)-3-phenylcyclopropanecarboxylic acid **2** as a mixture of two isomers and the product of methoxycarbonylcarbene insertion at the C-O bond – methyl ester of 3[(*E*)-2-phenylvinyl]-1,4-dioxane-2-carboxylic acid **3** as a mixture of two isomers are formed in the reaction of 2-[(*E*)-2-phenylvinyl]-1,3-dioxolane **1** with methyl diazoacetate in the presence of $Rh_2(OAc)_4$, and imidazolium salts, in contrast to the interaction of N_2CHCO_2Me with dioxolane **1** in the presence of $Rh_2(OAc)_4$,[15] with the total yield to 81% respectively (Table 1).



Scheme 1 – Interaction of 1,3-dioxa- and 1,3-oxatiolanes with N_2CHCO_2Me in the presence of $Rh_2(OAc)_4$.



Scheme 2 – Catalytic interaction 2-[(*E*)-2-phenylvinyl]-1,3-dioxolane with N_2CHCO_2Me

Table 1

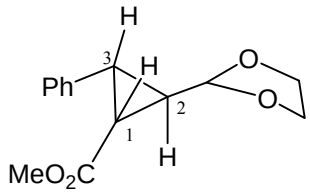
The influence of the catalyst type and imidazolium salts on the interaction of 2-[(*E*)-2-phenylvinyl]-1,3-dioxolane **2** with N_2CHCO_2Me

	Catalyst	Temperature, ºC	Yield, % (isomer ratio)	
			2 (1*r*,2*t*,3*c*)-/ (1*r*,2*c*,3*t*)-	**3** (*trans*-*: cis*-)
1	$Rh_2(OAc)_4$	40	-	47
2	$Rh_2(OAc)_4$-$[bmim]^+PF_6^-$	40	18 (2:1)	58 (4:1)
3	$Rh_2(OAc)_4$-$[bmim]^+BF_4^-$	40	15 (4:1)	60 (4:1)
4	$Rh_2(OAc)_4$-$[bmim]^+Cl^-$	40	14 (2:1)	50 (4:1)
5	$Cu(OTf)_2$	40	-	-
6	$Cu(OTf)_2$-$[bmim]^+PF_6^-$	40	23 (1:1)	58 (2:1)
7	$Cu(OTf)_2$-$[bmim]^+BF_4^-$	40	15 (2:1)	42 (3:1)
8	$Cu(OTf)_2$-$[bmim]^+Cl^-$	40	10 (2:1)	35 (3:1)
9	$Cu(OTf)_2$-$[bmim]^+PF_6^-$	75	10(3:1)	26 (2:1)
10	$Cu(OTf)_2$-$[bmim]^+BF_4^-$	75	15 (2:1)	24 (2:1)
11	$Cu(OTf)_2$-$[bmim]^+Cl^-$	75	8 (1:1)	15 (2:1)

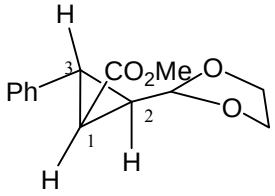
It should be noted that the use of $Cu(OTf)_2$ in this reaction was not effective. As in the case of cyclopropropanation of dioxolane **1** with diazomethane,[16] $Cu(OTf)_2$ catalyzes the acetal deprotection giving rise to the starting cinnamaldehyde.

Addition of 1 mol. % imidazolium salts $[bmim]^+X^-$ as cocatalyst leads to changing of pathway of the reaction. Such change of regioselectivity, most probably, is explained by the formation a new complex Rh(II) or Cu(II), which catalyses of cyclopropanation of the double bond C=C.[17] We have shown that use of the catalytic system $Rh_2(OAc)_4$-$[bmim]^+X^-$ or $Cu(OTf)_2$-$[bmim]^+X^-$ is effective for cyclopropanation of double bond C=C 5-allyloxy substitutes of 1,3-dioxanes and allyl-, *trans*- and *cis*-chloropropenyl butyl ethers by methyl diazoacetate.[18,19]

Methyl 2-(1,3-dioxolan-1-yl)-3-phenylcyclopropanecarboxylate **2** as a mixture of two isomers and products of methoxycarbonylcarbene insertion at the C-O bond - methyl of 3[(*E*)-2-phenylvinyl]-1,4-dioxane-2-carboxylate **3** were isolated by column chromatography from the reaction mixture. Structure of the obtained compounds was characterized by ^1H, ^{13}C NMR spectroscopy and c GC-mass spectrometry.



(1*r*,2*t*,3*c*)-**2**

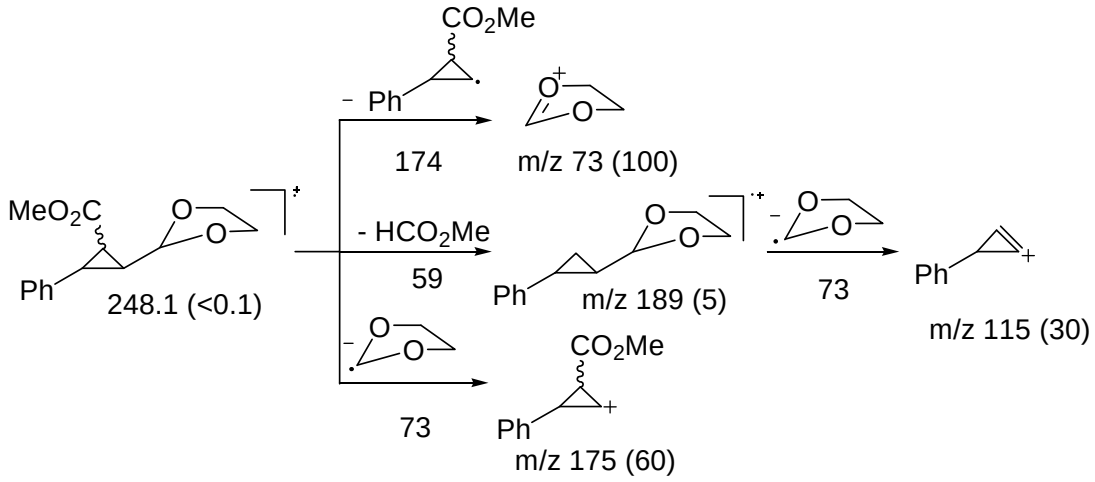


(1*r*,2*c*,3*t*)-**2**

Protons at C (1) and C (3) of the cyclopropane ring are characteristic in the ^1H NMR spectra for 1,2,3-trisubstituted cyclopropanes **2**. Protons at C (1) and C (3) atoms (1*r*,2*t*,3*c*)- isomer **2** resonate as a doublet of doublets in the region of δн 2.2 ppm ($^3J_{1\text{-}3}$ = 9.6 and $^3J_{1\text{-}2}$ = 5.2 Hz) and 2.71 ppm ($^3J_{2\text{-}3}$ = 7.1 and $^3J_{1\text{-}3}$ = 9.6 Hz), which corresponds to the *cis*-arrangement of methoxycarbonyl and phenyl groups. Similarly, for the (1*r*,2*c*,3*t*)- isomer **2** these protons are as a doublet of doublets in the regions of δн 2.15 ppm ($^3J_{1\text{-}2}$ = 9.0 and $^3J_{1\text{-}3}$ = 6.0 Hz) and triplet in the region of δн 2.80 ppm (^3J = 6.0 Hz), which are typical for the *trans*-arrangement of the substituents (CO_2Me and Ph) in the cyclopropane ring. The SSCC values of protons, at the C(1) and C(3) atoms of both isomers, point to *trans*-location of phenyl group and dioxolane fragment, which confirms the reaction cyclopropanation with the retention of the original double bond configuration C=C. These results are consistent with known data of reaction mechanism[5]. It should also be noticed that the signals of carbon atoms of cyclopropanes ring at C(2) of (1*r*,2*c*,3*t*)-isomer **2** and at C(1) и C(3) atoms of (1*r*,2*t*,3*c*) isomers resonate in the strong region of ^{13}C NMR spectra, that is characteristic for the *cis*-substituted cyclopropanes[20]. Isomer ratio of (1*r*,2*t*,3*c*)- / (1*r*,2*c*,3*t*)- was determined by the integral intensity of protons at C(3) of cyclopropanes ring δн 2.71 and 2.8 ppm respectively.

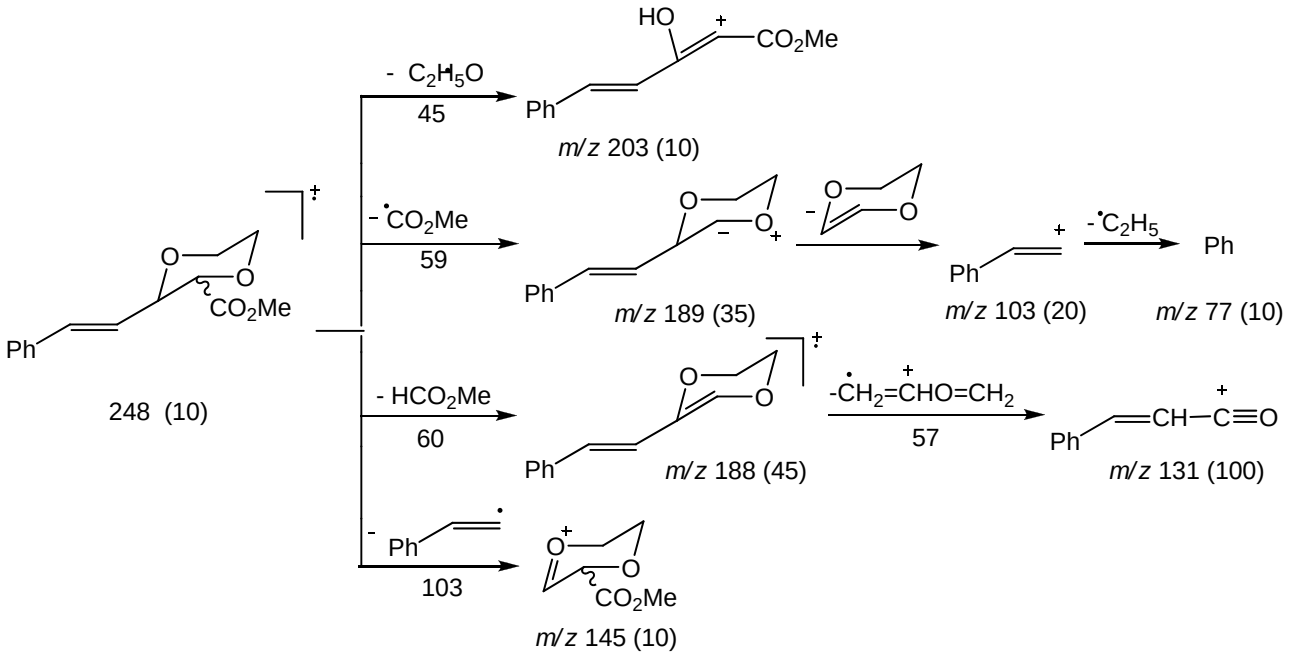
Correlation of *trans*-/*cis*-izomers of 2,3-disubstituted 1,4-dioxanes was followed on the basis of the chemical shifts of the proton signals in the ^1H NMR spectrum for the carbon atoms C (2) and C (3), associated with methoxycarbonyl and phenylethynyl groups. For *trans*-1,4-dioxane **3** doublet signals are in δн area 4.04 and 4.24 ppm ($^3J_{H(2)H(3)}$ = 8.8 Hz), and in the case of the *cis*-isomer **3** - at δ_H 3.95 and 4.10 ppm ($^3J_{H(2)H(3)}$ = 5.5 Hz), respectively. In the ^{13}C NMR spectrum there are characteristic signals of carbon atoms C (5) and C (6), which is in the α-position to the oxygen atoms of 1,4-dioxane moiety appear in δ_C 63.7 – 66.1 ppm.

Mass-spectrum (EI) of the 1,3-dioxolane **2** contains molecular ion peak less than 1% and fragment ion peak with m/z 73 (100%) that are typically for cyclic acetals (Scheme 3). The sequence of 1,3-dioxolane dissociation **2**, confirmed by unstable ions, is registered:



Scheme 3 – Scheme of dissociation of methyl 2-(1,3-dioxolan-2-yl)-3-phenyl-cyclopropanecarboxylate.

The fundamental distinction of mass-spectra (EI) 1,4-dioxane **3** from mass-spectra 1,3-dioxolane **2** is molecular ion peak (*m/z* 248) and series of fragment ion peaks, the most intensive peaks among them are due to removal C_2H_5O, methoxycarbonyl, ethyl and phenylvinyl groups (Scheme 4). The next sequence of dissociation of dioxane **6**, confirmed by metastable ion peaks, is registered:



Scheme 4 – Scheme of dissociation of methyl 3-[(*E*)-2-phenylvinyl]-1,4-dioxane-2-carboxylate.

Of special merit is the fact that obtaining cyclopropanation of double bond C=C is possible in the presence of the catalytic system $Cu(OTf)_2$-$[bmim]^+X^-$, while using copper (II) triflate in the reaction 2-(alke-1-nyl)-1,3-dioxa- and 1,3-oxathiolane with methyl diazoacetate is not effective. The results confirmed the provided data in the literature that the use of ionic liquid, most likely, is due to ligand exchange and the formed new complex that is effective catalyst of cyclopropanation of bond C=C.[17]

EXPERIMENTAL

General

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz respectively)

solvent $CDCl_3$, internal standard Me_4Si. An Chrom-5 chromatograph was used for the qualitative and quantitative analysis of starting material and reaction products. The chromatograph was equipped with a flame ionization detector (column is 1200-5 mm with 5% SE-30 on an Inerton N-AW DMCS (0.125–0.160 mm), a carrier gas – helium. TLC analysis was carried out on chromatographic layers Silufol of Merck company, preparatory separation carried out by the column chromatography, using silica gel Sigma-Aldrich (0.040–0.063 mm). Mass-spectra were recorded on a Thermo Finnigan MAT 95 XP (EI, 70 eV, ionization cell temperature 250°C, injector temperature 50–250°C, with a velocity of the temperature rise 10°C/min) and MX-1300 with insertion *via* a temperature balloon at 100°C with ionization energy of 12 and 70eV.

Commercially available 1-methylimidazole, 1-butyl chloride, $Rh_2(OAc)_4$, $Cu(OTf)_2$ – manufactured by "Aldrich"; cinnamaldehyde ("Acros" purity > 98%) were used in the work. Ionic liquids are prepared according to known methods.[21,22] Used solvents in the work (methylene chloride, 1,2-dichloroethane, petroleum ether (b.p. 40-70ºC.), ethyl acetate) were purified according to standard procedures.[23]

General procedure for the interaction of 2-((E)-2-phenylvinyl)-1,3-dioxolane with methyl diazoacetate in the presence of ionic liquid.

A solution of 0.1 g (1 mM) methyl diazoacetate in 5 mL solvent was added dropwise to the solution of 0.05 g (1 mM) unsaturated compound **1**, 0.01 mM ionic liquid and 0.01 mM catalyst comprising Cu or Rh in 5 mL methylene chloride at 40°C or 1,2-dichloroethane at 75°C and this is stirring for 3h with heating. After the completion of the reaction the solvent was evaporated under reduced pressure, petroleum ether was added to the residue (bp 40–70°C) and isolated the catalytic system as brown-black color oil. The solvent in petroleum ether was evaporated over low pressure, and the residue was analyzed chromatographically.

Methyl 2-(1,3-dioxolane-1-yl)-3-phenylcyclopropanecarboxylate (**2**)*:* the product was obtained as a mixture of isomers (1*r*,2*t*,3*c*)-/(1R*,2R*,3R*)- by column chromatography, R_f 0.36 (eluent – petroleum ether (b.p. 40-70ºC) – AcOEt, 7 : 3). MS (70eV), *m/z* (*I*, %): 248.1 M^+ (<0.1), 189 (5), 175 (60), 115 (30), 73 (100). M 248.1048.

(1*r*,2*t*,3*c*)-Isomer **2**. ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 1.85 (ddd, 1H, HC(2), ^3J 9.6, ^3J 7.1,^3J 3.7), 2.2 (dd, 1H, HC(1), ^3J 9.6, ^3J 5.2), 2.71 (dd, 1H, HC(3), ^3J 9.6, ^3J 7.1), 3.45 (s, 3H, OCH_3), 4.22-4.35 (m, 4H, $2CH_2$-O), 5.01 (d, 1H, HC(2'), ^3J 6.6), 7.27–7.35 (m, 5H, Ar). ^{13}C-NMR (δ ppm): 24.37 (C(1)), 27.11 (C(3)), 28.89 (C(2)), 52.02 (OMe), 64.89 and 65.76 (C(4') and C(5')), 102.71 (C(2')), 127.8-128.9 (5 CH, Ar), 136.16 (C, Ar), 170.19 ($\underline{C}O_2$).

(1*r*,2*c*,3*t*)-Isomer **2**. ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 2.15 (dd, 1H, HC(1), ^3J 9.0, ^3J 6.0), 2.4 (ddd, 1H, HC(2), ^3J 9.0, ^3J 6.0,^3J 7.4), 2.80 (t, 1H, HC(3), ^3J 6.0), 3.47 (s, 3H, OCH_3), 4.22-4.35 (m, 4H, $2CH_2$-O), 5.12 (d, 1H, HC(2'), ^3J 9.0), 7.27–7.35 (m, 5H, Ar). ^{13}C-NMR (δ ppm): 26.51 (C(1)), 27.99 (C(3)), 31.78 (C(2)), 52.16 (OMe), 64.98 and 65.84 (C(4') and C(5')), 102.82 (C(2')), 127.8-128.9 (5 CH, Ar), 136.04 (C, Ar), 170.43 ($\underline{C}O_2$).

Methyl 3-(trans-2-phenyl-ethenyl)-1,4-dioxane-2-carboxylate (**3**)*:* the product is separated by means of column chromatography, R_f 0.88 (eluent – petroleum-ether (b.p. 40-70ºC)-AcOEt, 7 : 3). MS (70eV), *m/z* (*I, %*): 248 M^+ (10), 203 (10),189 (35), 188 (45), 145 (10), 131 (100), 103 (20), 77 (10). *M* 248.1048. The compound **3** is mixture of *trans/cis*-isomers, slightly varying by location of NMR signals.

trans-Isomer **3**. ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 3.80 (s, 3H, OMe), 3.73-3.85 (m, 4H, $H_2C(5)$ and $H_2C(6)$), 4.04 (d, 1H, HC(2), ^3J 8.8), 4.25 (dd, 1H, HC(3), ^3J 7.1, ^3J 8.8), 6.15 (dd, 1H, HC(1`), $^3J$ 16.0, $^3J$ 6.9), 6.72 (d, 1H, HC(2`), ^3J 16.0), 7.27–7.35 (m, 5H, Ar). ^{13}C-NMR (δ ppm): 52.4 (OMe), 65.3, 65.4 (C(5) and C(6)), 77.2 (C(2)), 79.1 (C(3)), 123.5 (C(1`)), 133.5 (C(2`)), 127.8-128.9 (5 CH, Ar), 136.3 (C, Ar), 168.3 (COO).

cis-Isomer **3**. ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 3.79 (s, 3H, OMe), 3.73-3.85 (m, 4H, $H_2C(5)$ and $H_2C(6)$), 3.95 (d, 1H, HC(2), ^{3} *J* 5.5), 4.10 (dd, 1H, HC(3), ^3J 7.1, ^3J 5.5), 6.15 (dd, 1H, HC(1`), $^3J$ 16.0, $^3J$ 6.9), 6.72 (d, 1H, HC(2`), ^3J 16.0), 7.27–7.35 (m, 5H, Ar). ^{13}C-NMR (δ ppm): 51.7 (OMe); 64.7, 64.8 (C(5) and C(6)), 74.3 (C(2)), 75.8 (C(3)), 122.2 (C(1`)), 134.1 (C(2`)), 127.8-128.9 (5 CH, Ar), 136.3 (C, Ar), 168.5 ($\underline{C}O_2$).

CONCLUSIONS

Thus, the path way of the reaction of ethylene acetal **1** with methyl diazoacetate significantly depends on the nature of the used catalyst. Reaction proceeds with the formation of products of methoxycarbonylcarbene introduction on the C-O bond with the formation of six-and eight-membered heterocycles in case the use of $Rh_2(OAc)_4$. Application of imidazolium salts as cocatalysts allows to the cyclopropanation of the C=C bond and to obtain 1,2,3-trisubstituted cyclopropanecarboxylate. The obtained compounds could be of interest as multifunctional synthons for different chemical processes.

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