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Effect of Imidazolium Salts on the Catalytic Reaction of 1,3-Dioxolanes with Methyl Diazoacetate

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Abstract—Effect of imidazolium salts, $[\text{bmim}]^+\text{Cl}^-$, $[\text{bmim}]^+\text{BF}_4^-$, and $[\text{bmim}]^+\text{PF}_6^-$, on the reaction of 1,3-dioxolanes with methyl diazoacetate in the presence of copper-containing catalysts was studied. The product composition was found to depend on the reaction conditions and the nature and ratio of components of the catalytic system.

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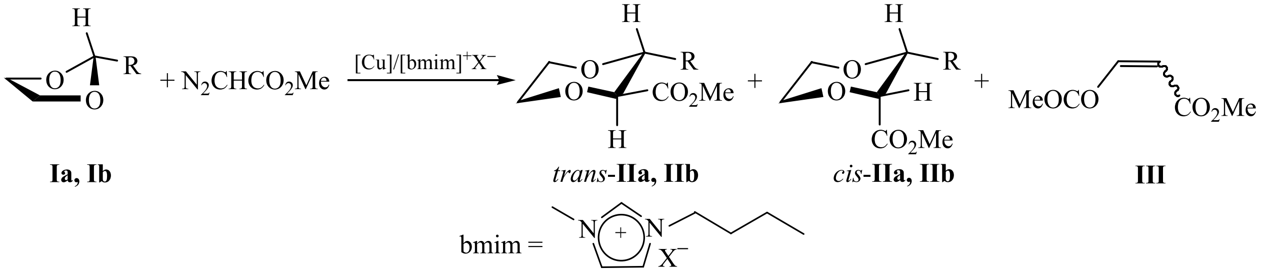
The ability of alkyl diazoacetates to form products of insertion into σ-bonds opens wide prospects in carbofunctionalization of compounds having no multiple bonds [1]. For example, reactions of homologs and heteroanalogs of 1,3-dioxolanes, such as 1,3-dioxanes, 1,3-oxazolidines, and 1,3-oxathiolanes, with methyl diazoacetate in the presence of $Rh_2(OAc)_4$ lead to the formation of formal insertion products of methoxycarbonylcarbene into carbon–heteroatom bond [2, 3]. The use in these reactions of copper compounds, e.g., $Cu(OTf)_2$ and $CuSO_4$, provides less satisfactory results [4]. On the other hand, it was noted [5] that ionic liquids based on imidazolium salts promote reactions catalyzed by Lewis acids, metal complexes, and organocatalysts.

In the present work we examined catalytic reactions of 2-isopropyl- and 2-phenyl-1,3-dioxolanes **Ia** and **Ib** (see table) with methyl diazoacetate and found that the use of imidazolium salts as co-catalysts increases the yield of methyl 1,4-dioxane-2-carboxylates to 30% and reduces the yield of methoxycarbonylcarbene dimerization products to 5–14%. The reactions were carried out in the temperature range from 25 to 75°C by adding a solution of methyl diazoacetate in methylene chloride or 1,2-dichloroethane to the corresponding 1,3-dioxolane containing catalyst, the molar ratio 1,3-dioxolane–methyl diazoacetate–catalyst–$[\text{bmim}]^+\text{X}^-$ being 1 : 1 : 0.01 : 0.01. As imidazolium salts we used $[\text{bmim}]^+\text{Cl}^-$, $[\text{bmim}]^+\text{BF}_4^-$, and $[\text{bmim}]^+\text{PF}_6^-$, and various copper, rhodium, and ruthenium compounds were tried as catalyst [$Cu(OAc)_2$, $CuOTf\cdot C_6H_6$, $Cu(OTf)_2$, $Rh_2(CF_3CO_2)_4$, $Rh_2(OAc)_4$, $Ru_2(OAc)_4Cl$]. It was found that in the presence of $[\text{bmim}]^+\text{PF}_6^-$ the most effective were $Cu(OTf)_2$ and $Cu(acac)_2$. No reaction occurred between methyl diazoacetate and 1,3-



R= *i*-Pr (**a**), Ph (**b**); X = Cl, BF_4, PF_6.

Reaction of 1,3-dioxolanes **Ia** and **Ib** with methyl diazoacetate[a]

Initial 1,3-dioxolane no.	Catalyst	Temperature, °C	Yield, % (*trans–cis* ratio)		
			II	**III**	aldehyde
Ia	$Cu(OTf)_2/[bmim]^+ PF_6^-$	40	–	36 (3:1)	–
	$Cu(acac)_2/[bmim]^+ Cl^-$		–	99 (1:1)	–
	$Cu(acac)_2/[bmim]^+ BF_4^-$		5 (1:1)	95 (3:1)	–
	$Cu(acac)_2/[bmim]^+ PF_6^-$		42 (6:1)	58 (3:1)	–
	$Cu(acac)_2/[bmim]^+ Cl^-$	75	–	99 (1:1)	–
	$Cu(acac)_2/[bmim]^+ BF_4^-$		13 (3:1)	87 (2:1)	–
	$Cu(acac)_2/[bmim]^+ PF_6^-$		6 (2:1)	94 (1:1)	–
Ib	$Cu(OTf)_2/[bmim]^+ Cl^-$	25	9 (2:1)	41 (1:1)	8
	$Cu(OTf)_2/[bmim]^+ BF_4^-$		25 (2:1)	14 (1:1)	15
	$Cu(OTf)_2/[bmim]^+ PF_6^-$		7 (2:1)	12 (2:1)	14
	$Cu(OTf)_2/[bmim]^+ Cl^-$	40	14 (2:1)	14 (1:1)	24
	$Cu(OTf)_2/[bmim]^+ BF_4^-$		25 (6:1)	5 (4:1)	8
	$Cu(OTf)_2/[bmim]^+ PF_6^-$		30 (6:1)	12 (3:1)	6
	$Cu(OTf)_2/[bmim]^+ PF_6^-$[b]		54 (3:1)	24 (2:1)	10
	$Cu(OTf)_2/[bmim]^+ Cl^-$	75	19 (6:1)	3 (2:1)	18
	$Cu(OTf)_2/[bmim]^+ BF_4^-$		24 (4:1)	9 (2:1)	42

[a] Molar ratio dioxolane **I**–N_2CHCO_2Me–[Cu]–$[bmim]^+X^-$ 100 : 100 : 1 : 1; reaction time 24 h. [b] Molar ratio dioxolane **I**–N_2CHCO_2Me–[Cu]–$[bmim]^+X^-$ 100 : 200 : 1 : 1. Excess methyl diazoacetate decomposed to give dimethyl fumarate, dimethyl maleate, and higher oligomers.

dioxolanes **Ia** and **Ib** if any of the above components was absent. It should also be noted that we detected no products of insertion of methoxycarbonylcarbene into C–H or O^3–C^4 bonds in 1,3-dioxolanes. Neither 2-dichloromethyl-2-isopropropyl- nor 2-dichloromethyl-2-phenyl-1,3-dioxolane reacted with methyl diazoacetate under analogous conditions.

The reaction of 2-phenyl-1,3-dioxolane (**Ib**) with methyl diazoacetate in the presence of $Cu(OTf)_2$ and $[bmim]^+PF_6^-$ at 40°C gave a mixture of *cis*- and *trans*-isomeric methyl 3-phenyl-1,4-dioxane-2-carboxylates at a ratio of 1 : 6 in an overall yield of 30%. The best results were obtained at 40°C. At 25°C the yield of stereoisomeric esters **IIb** did not exceed 25% (*trans–cis* ratio 2 : 1), whereas at 75°C the main process was decomposition of initial acetal **Ib** to benzaldehyde, which is consistent with the data of [6]. Such ionic liquids as $[bmim]^+BF_4^-$ and $[bmim]^+PF_6^-$ ensured maximal stereoselectivity in the carbene insertion process (*trans–cis* ratio 6 : 1). According to published data [7], the reaction of acetal **Ib** with methyl diazoacetate in the presence of $Rh_2(OAc)_4$ afforded only *trans* isomer **IIb**. In our experiments, both *cis* and *trans* isomers were obtained, and their yield and ratio depended on the ionic liquid used.

Insertion of alkoxycarbonylcarbenes into acetal **Ia** was successful only in the presence of $Cu(acac)_2$ at 40 and 75°C. Among the examined ionic liquids, $[bmim]^+PF_6^-$ turned out to ensure the best results: the yield of stereoisomeric esters **IIa** was 42%, and the *trans–cis* ratio was 6 : 1. Presumably, at 75°C the catalyst primarily promotes dimerization of alkoxycarbonylcarbene (the yield of esters **III** considerably increases), while the insertion process with formation of stereoisomeric esters **IIa** is characterized by a poor yield (6–13%).

The yields and isomeric compositions of the products formed by reactions of 1,3-dioxolanes **Ia** and **Ib** with methyl diazoacetate were determined by NMR spectroscopy. The stereoisomer ratio of 1,4-dioxanes **IIa** and **IIb** was calculated from the intensities of signals from protons at the C^2 and C^3 atoms. Doublet signals at δ 4.59 and 4.62 ppm in the ^1H NMR spectrum of **IIb** were assigned to protons on C^2 and C^3 linked to the methoxycarbonyl and phenyl groups, respectively, in the *trans* isomer. The vicinal coupling constant $^3J_{HH}$ equal to 8.8 Hz indicated axial orientation of both 2-H and 3-H and hence equatorial orientation of the methoxycarbonyl and phenyl groups. The doublets at δ 4.56 and 4.57 ppm were assigned to 2-H and 3-H, respectively, in the *cis* isomer; the corresponding coupling constant $^3J_{HH}$ was 4.2 Hz.

In the ^{13}C NMR spectrum of compound **IIb**, signals from C^2 and C^3 of the *trans* isomer were located in a weaker field relative to the corresponding signals of the *cis* isomer: their chemical shifts are δ_C 80.9, 80.0 ppm (*trans*) and 75.7, 74.7 ppm (*cis*).

The formation of the *trans* isomer of **IIb** is preferred. Analogous relation is observed for 1,4-dioxane **IIa**. Protons on C^2 and C^3 in *trans*-**IIa** (linked to the methoxycarbonyl and isopropyl groups, respectively) resonated as multiplets at δ 3.75 and 3.2 ppm, and multiplet signals at δ 3.7 and 3.23 ppm were assigned to 2-H and 3-H in the *cis* isomer. In the ^{13}C NMR spectrum of stereoisomer mixture *trans*-**IIa**/*cis*-**IIa**, signals from C^2 and C^3 of the *trans* isomer (δ_C 73.4, 79.6 ppm) appeared in a weaker field relative to those of the *cis* isomer (δ_C 76.1, 79.2 ppm).

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The reaction mixtures were analyzed by gas–liquid chromatography on a Shimadzu GC-2014 instrument equipped with a flame ionization detector and a 25-m DB-35MS capillary column; carrier gas helium. Initial 1,3-dioxanes **Ia** and **Ib** were synthesized according to the procedure described in [8], distilled in a stream of argon, and stored in an inert atmosphere over metallic sodium; the solvents used were purified by standard methods [9].

Catalytic reaction of 1,3-dioxolanes **Ia** and **Ib** with methyl diazoacetate (*general procedure*). Dioxolane **Ia** or **Ib**, 1.3 mmol, was added to a solution of 0.013 mmol of the corresponding copper catalyst and 0.013 mmol of ionic liquid in 5 ml of methylene chloride CH_2Cl_2, the mixture was heated to 40°C, and a solution of 1.3 mmol of methyl diazoacetate in 5 ml of methylene chloride was slowly added dropwise under stirring until gaseous products no longer evolved. After 3 h, the solvent was removed under reduced pressure, petroleum ether (bp 40–70°C) was added to the residue, and the catalytic system was separated as a dark brown oil. The solution in petroleum ether was evaporated under reduced pressure. The yields of the products were determined from the ^1H NMR spectra using CH_2Cl_2 as internal reference. The spectral parameters of compounds **IIa** and **IIb** were consistent with those reported [4].

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