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Catalytic Cyclopropanation of Stereoisomeric 1,3-Dichloropropenes with Methyl Diazoacetate

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Abstract—The catalytic cyclopropanation of *cis*- and *trans*-1,3-dichlorpropenes with methyl diazoacetate in the presence of a copper catalyst was studied. The products composition and ratio were shown to depend on the spatial structure of 1,3-dichloropropene.

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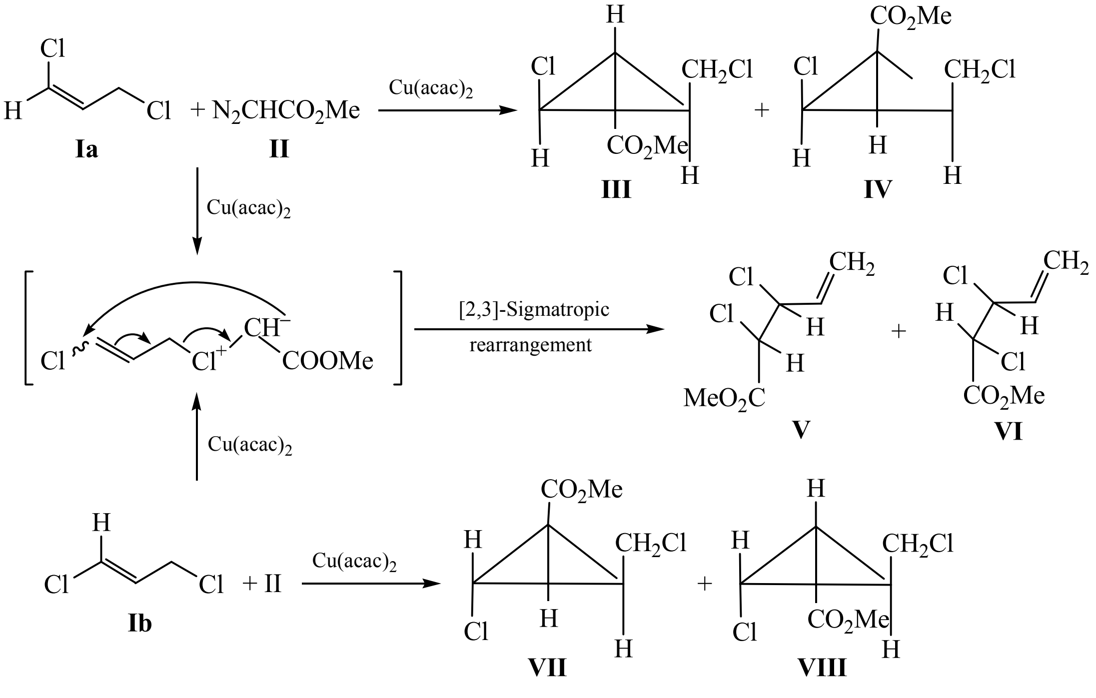
The *cis*- and *trans*-1,3-dichloropropenes **Ia** and **Ib** are the major by-products in the allyl chloride production [1]. The isolation of isomers **Ia** and **Ib** by distilling the mixture has been described earlier [2]. The unsaturated compounds **Ia** and **Ib** are of interest as promising reagents for the fine organic synthesis.

The reactions of allyl halides with alkyl diazoacetates in the presence of copper and rhodium catalysts were known to give both the C–X- and cyclopropane adducts [3]. In the present work the reaction of *cis*-and *trans*-1,3-dichloropropenes **Ia** and **Ib** with methyl diazoacetate in the presence of Cu(acac)$_2$ was examined.

The catalytic cyclopropanation of isomers **Ia** and **Ib** with methyl diazoacetate results in both carbocyclic compounds, the methyl cyclopropanecarboxylates as a mixture of *cis*- and *trans*-isomers **III**, **IV** and **VII**, **VIII,** and linear products, the diastereomeric methyl 2,3-dichloropent-4-enoates **V** and **VI** (see the table).

Starting from *cis*-isomer **Ia**, cyclopropanes **III** and **IV** are formed in amounts comparable to amounts of the linear esters **V** and **VI**. The predominance of



isomer **III** in a mixture is due to the fact that the cyclopropanation of the double bond occurs predominantly from the sterically least hindered side [4].

The reaction of *trans*-isomer **Ib** occurs as a [2,3]-sigmatropic rearrangement [5] to form the linear diastereomers **V** and **VI** in overall yield of 60%. The reaction mixture contained also methyl cyclopropanecarboxylates **VII** and **VIII**.

Note that the products of the insertion of methoxycarbonylcarbenes into the allylic C–Cl bond, which are the main product in the case of allyl chloride [3], were not found. This is probably due to the fact that the chlorine atom at the double bond greatly reduces donor ability of the latter, which limits the mobility of the halogen atom in the CH_2Cl-group.

The mixtures of *trans*-/*cis*-isomeric cyclopropanes [**III** + **IV**] and [**VII** + **VIII**], and the diastereomers [**V** + **VI**] were isolated from the reaction mixture by the column chromatography. Their structure was proved by the ^{1}H NMR and GC-MS methods. Thus, the signal of the proton at the cyclopropane ring carbon associated with the methoxycarbonyl group in the *trans*-isomer **III** is registered at 1.89 ppm as a doublet of doublets with the spin-spin coupling constants $^3J_{1\text{-}3}$ 5.7 and $^3J_{1\text{-}2}$ 3.5 Hz, whereas the same signal of the proton in the *cis*-isomer **IV** is in a weaker field (1.92 ppm, $^3J_{1\text{-}3}$ 9.0 and $^3J_{1\text{-}2}$ 8.0 Hz). A multiplet signal of the proton in cyclopropane ring at CH_2Cl-group in the *trans*-isomer **III** is located in a stronger field (2.07 ppm) than for the same proton in the *cis*-isomer **IV** (2.15 ppm). The proton of cyclopropane ring at the chlorine atom in the *trans*-isomer **III** is manifested as a doublet of doublets at 3.63 ppm with the spin-spin coupling constants $^3J_{2\text{-}3}$ 7.6 and $^3J_{2\text{-}1}$ 3.5 Hz, whereas the same proton signal in the *cis*-isomer **IV** is a triplet in a stronger field (3.57 ppm, $^3J_{2\text{-}1}$ and $^3J_{2\text{-}3}$ 8.0 Hz).

The proton signal of CH-group of cyclopropane ring associated with the methoxycarbonyl moiety in compound **VII** is observed at 2.26 ppm ($^3J_{1\text{-}2}$ 3.8 and $^3J_{1\text{-}3}$ 10.0 Hz), whereas the signal of the same proton in isomer **VIII** is in a weaker field (2.32 ppm, $^3J_{1\text{-}3}$ 4.0, $^3J_{1\text{-}2}$ 7.8 Hz). The proton of cyclopropane ring carbon bound to the chlorine atom in compound **VII** is observed as a triplet signal at 3.45 ppm with the spin-spin coupling constants $^3J_{2\text{-}3}$ and $^3J_{2\text{-}1}$ 3.88 Hz. The similar proton in compound **VIII** is manifested as a doublet of doublets at 3.61 ppm ($^3J_{2\text{-}1}$ 7.8, $^3J_{2\text{-}3}$ 4.0 Hz). The multiplet signals of the CH_2Cl-protons at the cyclopropane ring of compounds **VII** and **VIII** are registered at 2.08 and 2.15 ppm, respectively.

Yields of the products of the reaction of *cis*- and *trans*-1,3-dichloropropenes **I** with methyl diazoacetate[a]

Compound	Yield, % (isomers ratio)		
	III+IV	**V+VI**	**VII+VIII**
Ia	42 (8:1)	23 (1:1)	–
Ib	–	60 (1.5:1)	7 (5:1)

[a] The molar ratio olefin:N_2CHCO_2Me:catalyst is 7:1:0.01, solvent dichloroethane, *T* = 75°C.

In the ^{1}H NMR spectrum of a [**V** + **VI**] mixture a doublet of doublets at 4.77 ppm ($^3J_{3\text{-}4}$ 8.3 and $^3J_{3\text{-}2}$ 5.9Hz) belongs to the proton of CHCl-group near the double bond in compound **V**. The triplet observed in the ^{1}H NMR spectrum at 4.66 ppm ($^3J_{3\text{-}4}$ and $^3J_{3\text{-}2}$ 9.5 Hz) belongs to the similar proton in compound **VI**. The proton of CHCl group associated with methoxycarbonyl moiety in compound **V** resonates as a doublet (δ_H 4.48 ppm, ^3J 5.9 Hz), while the similar proton signal of compound **VI** appears in a stronger field (δ_H 4.29 ppm, ^3J 9.5 Hz). The values of the spin-spin coupling constants between two protons of CHCl-groups (5.9 and 9.5 Hz [6]) indicate the relative position of the protons on one side of the C–C bond (*erythro*-diastereomer) or on the different sides of this bond (*threo*-diastereomer), respectively. The chemical shifts values of the singlet signals of methoxy groups differ slightly and appear at 3.85 and 3.82 ppm in the *threo*- and *erythro*-diastereomers, respectively.

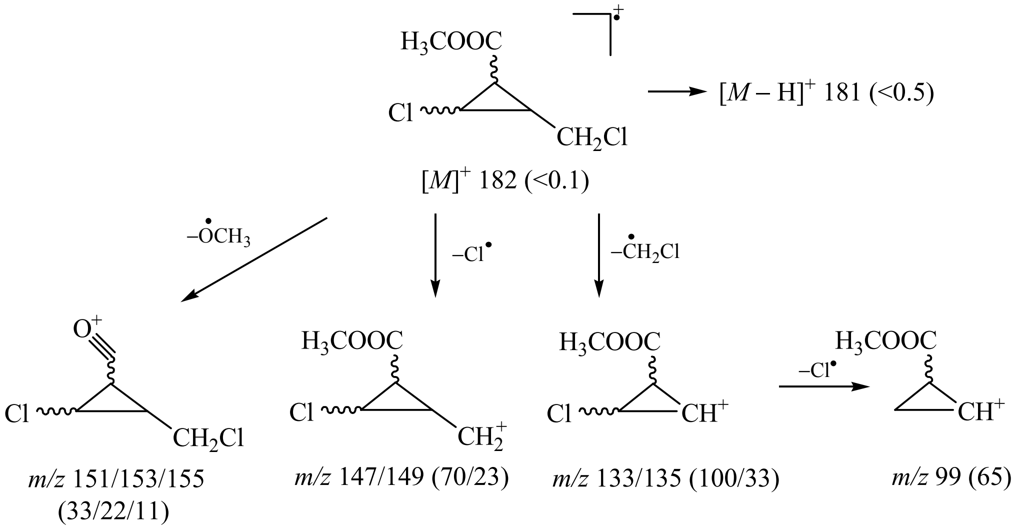
In the mass spectra of compounds **III**/**IV** and **VII**/**VIII** there are no molecular ions (Scheme 1). Their fragmentation proceeds similarly for the *cis*- and *trans*-isomers. The most intensive peaks are the ions with *m*/*z* 133/135 (100%).

The mass spectra of diastereomers **V**/**IV** also contain no molecular ions (Scheme 2). The maximum intensive fragment of isomers **V**/**IV** is a cation with *m*/*z* 147/149 (100%) formed by the chlorine atom cleavage. The dissociation proceeds similarly for the *erythro*- and *threo*-diastereomers **V** and **IV**.

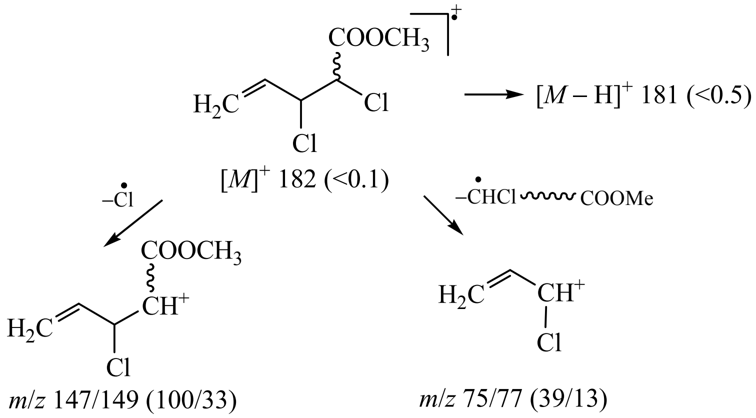
EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were registered on a Bruker AM 300 spectrometer (300.13 and 75.47 MHz, respectively) in $CDCl_3$ relative to internal Me_4Si. The mass spectra were recorded on a Thermo Finnigan MAT 95 XP mass-spectrometer (EI, 70 eV, ionization

Scheme 1.



Scheme 2.



chamber temperature 250°C, temperature of the direct injection 50–250°C, heating rate 10 deg min^{-1}). The GLC analysis was performed on a Shimadzu GC-2014 chromatograph with a flame ionization detector (capillary column DB35MS 25 m), carrier-gas helium). The TLC analysis was performed using Silufol chromatographic plates (Merck) eluting with a petroleum ether–AcOEt mixture (7:3). The preparative separation was performed by the column chromatography on silica gel (eluent petroleum ether with ethyl acetate content increasing from 5 to 100%). The used catalyst $Cu(acac)_2$ is a commercial product.

Catalytic reaction of 1,3-dichloropropenes with methyl diazoacetate *(general procedure).* To a stirred solution of 0.02 mmol of the catalyst in 3 ml of dichloroethane was added 14 mmol (1.5 g) of 1,3-dichloropropene followed by slow addition of 2 mmol (0.2 g) of methyl diazoacetate in 5 ml of dichloroethane at 75°C. After 3 h the reaction mixture was passed through a thin layer of Al_2O_3, the solvent was removed in a vacuum, and the residue was chromatographed on SiO_2.

Methyl 2-(*E*)-chloro-3-(*E*)-(chloromethyl)cyclopropanecarboxylate (III). R_f 0.40. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.88 d.d (1H, C^1H, $^3J_{1\text{-}3}$ 5.7, $^3J_{1\text{-}2}$ 3.5), 2.07 m (1H, C^3H), 3.63 d.d (1H, C^2HCl, $^3J_{2\text{-}3}$ 7.6, $^3J_{2\text{-}1}$ 3.5), 3.71 d.d (1H, CH_2Cl, ^2J 11.5, ^3J 6.8), 3.74 s (3H, OCH_3), 3.75 d.d (1H, CH_2Cl, ^2J 11.5, ^3J 6.8). ^{13}C NMR spectrum, δ_C, ppm: 170.32 (C=O), 52.29 (OCH_3), 41.60 (CH_2Cl), 38.77 (C^2HCl), 29.73 (C^1H), 28.97 (C^3H). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 182 (<0.1), 151/153/155 (33/22/11), 147/149 (70/23), 133/135 (100/33), 99 (65), 89 (40), 59 (45).

Methyl 2-(*Z*)-chloro-3-(*Z*)-(chloromethyl)cyclopropanecarboxylate (IV). R_f 0.40. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.92 d.d (1H, C^1H, $^3J_{1\text{-}3}$ 9.0, $^3J_{1\text{-}2}$ 8.0), 2.15 m (1H, C^3H), 3.57 t (1H, C^2HCl, $^3J_{2\text{-}3} = {^3J_{2\text{-}1}}$ 8.0), 3.71–3.82 m (2H, CH_2Cl), 3.76 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 170.30 (C=O), 52.02 (OCH_3), 38.85 (CH_2Cl), 36.13 (C^2HCl), 25.78 (C^1H), 23.96 (C^3H). Mass spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 182 (<0.1, 151/153/155 (33/22/11), 147/149 (70/23), 133/135 (100/33), 99 (65), 89 (40), 59 (45).

Methyl 2,3-dichloropent-4-enoate (V, VI). R_f 0.47. *erythro*-Diastereomer. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.82 s (3H, OCH_3), 4.48 d (1H, C^2HCl, ^3J 5.9), 4.77 d.d (1H, C^3HCl, ^3J 8.3, 5.9), 5.35 d.d.d (1H, C^4H=, ^3J 16.8, 10.5, 8.3), 5.95–6.07 m (2H, C^5H_2). ^{13}C NMR spectrum, δ_C, ppm: 166.70 (C=O), 133.09 (C^4H=), 120.33 (C^5H_2), 60.62 (C^3HCl), 58.32 (C^2HCl), 53.14 (OCH_3). *threo*-Diastereomer. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.85 s (3H, OCH_3), 4.29 d (1H, C^2HCl, ^3J 9.5), 4.70 t (1H, C^3HCl, ^3J 9.5, 9.5), 5.47 d.d.d (1H, C^4H=, ^3J 16.1, 10.0, 9.5), 5.95–6.07 m (2H, C^5H_2). ^{13}C NMR spectrum, δ_C, ppm: 166.72 (C=O), 133.32 (C^4H=), 121.20 (C^5H_2), 61.94 (C^3HCl), 60.44 (C^2HCl), 53.14 (OCH_3). Mass spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 182 (<0.1), 147/149 (100/33), 75/77 (39/13), 59 (14).

Methyl 2-(*E*)-chloro-3-(*Z*)-(chloromethyl)cyclopropanecarboxylate (VII). R_f 0.36. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.08 m (1H, C^3H), 2.26 d.d (1H, C^1H, $^3J_{1\text{-}3}$ 10.0, $^3J_{1\text{-}2}$ 3.8), 3.45 t (1H, C^2HCl, $^3J_{2\text{-}3}$, $^3J_{2\text{-}1}$ 3.8), 3.70 s (3H, OCH_3), 3.67 d (2H, CH_2Cl, ^3J 4.7). ^{13}C NMR spectrum, δ_C, ppm: 171.97 (C=O), 52.18 (OCH_3), 42.26 (CH_2Cl), 41.97 (C^2HCl), 29.43 (C^1H), 29.37 (C^3H). Mass spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 182 (<0.1), 151/153/155 (33/22/11), 147/149 (70/23), 133/135 (100/33), 99 (65), 89 (40), 59 (45).

Methyl 2-(*Z*)-chloro-3-(*E*)-(chloromethyl)cyclopropanecarboxylate (VIII). R_f 0.36. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.15 m (1H, C^3H), 2.32 d.d (1H, C^1H, $^3J_{1\text{-}3}$ 4.0, $^3J_{1\text{-}2}$ 7.8), 3.61 d.d (1H, C^2HCl, $^3J_{2\text{-}3}$ 4.0, $^3J_{2\text{-}1}$ 7.8), 3.72 s (3H, OCH_3), 3.60 d (2H, CH_2Cl, ^3J 5.2). ^{13}C NMR spectrum, δ_C, ppm: 171.95 (C=O), 52.02 (OCH_3), 42.12 (CH_2Cl), 41.97 (C^2HCl), 29.38 (C^1H), 29.26 (C^3H). Mass spectrum, *m*/*z* (I_{rel}, %): $[M]^+$ 182 (<0.1), 151/153/155 (33/22/11), 147/149 (70/23), 133/135 (100/33), 99 (65), 89 (40), 59 (45).

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