FORMATION OF 2-VINYLCYCLOPROPANECARBOXYLIC ACID ESTERS IN REACTIONS OF ALKYL DIAZOACETATES WITH GASEOUS DIVINYL AND SYNTHESIS OF 2-ETHYNYLCYCLOPROPANECARBOXYLIC ACID FROM THEM

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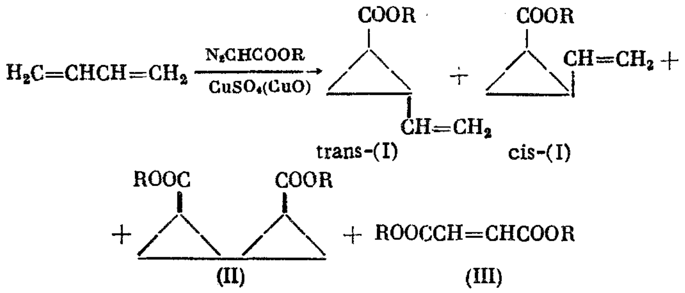
Esters of 2-alkenylcyclopropanecarboxylic acids are widely used as monomers [1] and intermediates in the synthesis of synthetic pyrethrins [2]. The existing laboratory and industrial methods for the preparation of these compounds, in particular, esters of chrysanthemic acid [3], are preferentially based on the liquid-phase catalytic reactions of alkyl diazoacetates (ADA) with dienic hydrocarbons. However, the simplest representative of this series, the ethyl ester of 2-vinylcyclopropanecarboxylic acid (Ic), can be obtained by this method in a yield of not more than 35% [4], and the process is carried out under pressure.

By using a previously developed method for carrying out the reaction of gaseous olefins with ADA [5], we were able to synthesize compounds (I) by passing a vapor—gas mixture of ADA with an excess of divinyl through a tubular continuous-flow reactor at atmospheric pressure and at an elevated temperature. Table 1 shows the results of the reaction of divinyl with methyl diazoacetate (MDA) and ethyl diazoacetate (EDA) at 65-200°C in the presence of CuO and $CuSO_4$ deposited in an amount of ∿ 10% on pumice. The contact time (τ_c) when using $CuSO_4$ was 3.6 sec, and with CuO, 5 sec. Under these conditions, with complete conversion of ADA, the reaction products were the corresponding esters of trans- and cis-(I), isomeric dicyclopropyl-2,2'-dicarboxylic acids (II), fumaric and maleic acids (III), with the ratio between them being dependent on the ADA and the type of the catalyst used (see Table 1). A change in the reaction temperature within the above limits has little influence on the yields and the ratio between the reaction products.



R=H (a), CH_3 (b), C_2H_5 (c)

TABLE 1. Composition of Products of the Reaction of Divinyl with Alkyl Diazoacetates (molar ratio of divinyl to diazoacetate 90-100 : 1, continuous flow reactor)

Compound	Yield, %, depending on the experimental conditions		Compound	Yield, %, depending on the experimental conditions	
	$CuSO_4$, 65—110°, 3,6 sec	CuO, 85—200°, 5 sec		$CuSO_4$, 65—110°, 3,6 sec	CuO, 85—200° 5 sec
trans-(Ib)	22–26	25–30	trans-(Ic)	14–18	22–25
cis-(Ib)	17–20	19–23	cis-(Ic)	10–14	17–20
(IIb)	10–12	5–6	(IIc)	8–10	2–4
(IIIb)	8–10	5–6	(IIIc)	12–14	6–10

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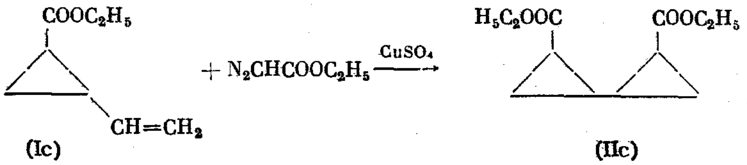
The maximal yields of the esters (I) were observed with MDA, reaching a total of 50% in experiments with CuO at 120-150°C. In all cases the isomer with the shorter retention time during the GLC predominated in the mixture of (I) formed (ratio between the isomers was 1.2-1.4 : 1); according to [4] this was a trans-isomer. By preparative GLC, the isomeric Ic were isolated in the pure state, and the accuracy of the assignment of the structure was confirmed by comparing their IR, PMR and mass spectra with the data of [6].

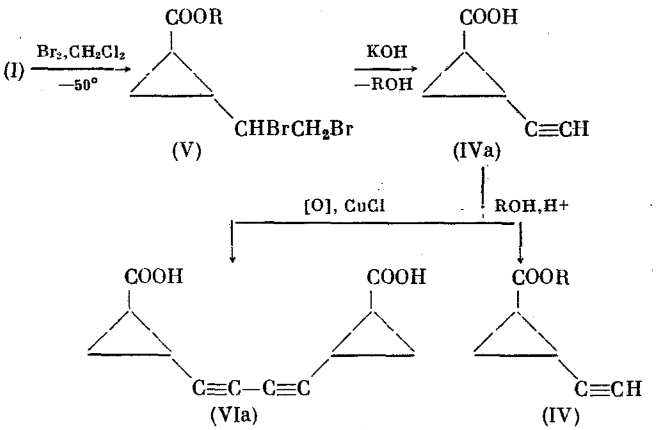
The mixture of isomers of (II) should theoretically consist of four geometrical and a large number of stereoisomers. Because of the low yield of the products, it was not possible to isolate them in a pure state, and therefore the mixture of (IIc) was identified by comparing the spectra and the retention times of the mixture components (during GLC) with those of a sample obtained in the reaction of EDA with a mixture of isomeric (Ic) in the presence of $CuSO_4$:



Under the continuous flow reactor conditions, the diester (II), like (III), is apparently formed during the reaction of ADA with alkoxycarbonylcarbene on the surface of the catalyst, since, if we take into account the high dilution of the reaction mixture with divinyl, bimolecular reactions with the participation of the end products or the intermediate particles in the free space are not probable.

Thus, under the conditions found for carrying out the reaction of ADA with divinyl, esters (I) can be obtained in a yield which is 1.5 times that formed in the best of the methods described in the literature for the preparation of these compounds [4]. We should note the high selectivity of the process, so that the product emerging from the reactor can be used for further transformations without additional purification. We could thus carry out a simple synthesis of 2-ethynylcyclopropanecarboxylic acid (IVa) and its esters, which according to [8], can be used for the synthesis of various carbofunctional cyclopropane derivatives with acetylenic groups in the molecule, which are important in practice. Up to the present time, compound (IV) was obtained by a multistage scheme in a total yield of ⩽ 20% [8].

According to our method CH_2Cl_2 solutions of esters (Ib), (Ic), or (Ia) obtained by their saponification with NaOH are brominated at −50°C. As a result, esters of 2-(1,2-dibromoethyl)cyclopropanecarboxylic acid (V) or acid (Va) are formed in yields up to 95%; their dehydrobromination leads to (IVa) in a yield of up to 50%. The esterification of (IVa) with alcohols in the presence of H_2SO_4 gives the corresponding esters (IVb, c):



R = H (a), CH_3 (b), C_2H_5 (c)

By oxidative dimerization in the presence of CuCl, acid (IVa) was converted into a previously unknown bis(2-carboxycyclopropyl)diacetylene (VIa) in a yield of up to 50%.

EXPERIMENTAL

The GLC analysis was carried out on the LKhM-8MD apparatus with a catharometer on a 3 m × 2 mm column with 15% of Carbowax on Chromaton N-AW-DMCS under conditions of matrix temperature programming (100-180°C); carrier gas helium, 30 ml/min. The individual compounds were isolated by preparative GLC on the PAKhV-8-0.5 apparatus, using a 4 m × 12 mm column with 15% 20M Carbowax on Chromaton N-AW-DMCS (0.25-0.36 mm). The PMR spectra were run on the "Varian DA-60-IL" apparatus, using TMS as the internal standard, the IR spectra on the UR-10 apparatus, and the mass spectra on the CH-6 apparatus with an ionizing-electron energy of 70 eV.

The initial ADA were prepared by the method given in [9] and contained 1-5% of the corresponding monochloroacetic acid ester, which passed unchanged into the reaction products.

The reactions of ADA with divinyl were carried out in an apparatus which we have described in [5].

Alkyl Esters of trans- and 2-cis-Vinylcyclopropane Carboxylic Acid (I). A vapor – gaseous mixture of 10.4 g (0.104 mole) of methyl diazoacetate and 213 liter (9.5 mole) of divinyl emerging from a vaporizer heated to 33°C was passed for 85 h through a quartz reactor heated to 135°C with an internal diameter of 1.8 cm, filled with 35 cm^3 pumice pieces, 1-2 mm in size, with 10% of CuO. In the receiver cooled to – 5°C, 8.2 g of catalyzate was collected. According to GLC, this contained 45% of trans-(Ib), 37% of cis-(Ib), 10% of a mixture of methyl esters of the isomeric dicyclopropyl-2,2'-dicarboxylic acids (IIb), 6% of methyl esters of fumaric and maleic acids (IIIb), and 2% of unidentified admixtures. The catalyzate was distilled, and 6.6 g (52%) of a mixture of trans-(Ib) and cis-(Ib), bp 62-70°C (25 mm) [IR spectrum (ν, cm^{-1}): 1640 (C=C), 1730 (C=O); PMR spectrum (in CCl_4, δ, ppm): 6.1-4.8 m (3H, $CH=CH_2$), 3.65 s (3H, OCH_3), 0.8-2.2 m (4H, ring protons); mol. wt. 126 (mass spectrometrically)] and 1 g (5%) of (IIb), bp 130-155°C (15 mm) [IR spectrum (ν, cm^{-1}): 1725 (C=O); PMR spectrum (in CCl_4, δ, ppm): 3.65, 3.64, 3.62, 3.60 four s (3H, OCH of the isomers), 0.5-2.0 (8H, ring protons); mol. wt. 198 (mass spectrometrically)] were obtained.

Similarly, a mixture of trans- and cis-(Ic), bp 68-72°C (14 mm), whose IR, PMR, and mass spectra were identical with the data of [6], and (IIc), bp 108-110°C (3 mm) [IR spectrum (ν, cm^{-1}): 1725 (C=O); mol. wt. 226 (mass spectrometrically)] were obtained. Isomers of (Ic), ∿100% pure, were isolated from the mixture by preparative GLC (180°C): trans-(Ic), IR spectrum (ν, cm^{-1}): 1640 (C=C), 1725 (C=O); PMR spectrum (CCl_4, δ, ppm): 4.8-5.7 (3H, $CH=CH_2$), 4.1 q (2H, OCH_2), 0.8-2.2 m (4H, ring protons), 1.27 t (3H, CH_3), $J_{OCH_2-CH_3}$ = 7 Hz; mol. wt. 140 (mass-spectrometrically), cis-(Ic), IR spectrum (ν, cm^{-1}): 1640 (C=C), 1725 (C=O); PMR spectrum (CCl_4, δ, ppm): 4.8-6.0 m (3H, $CH=CH_2$), 4.05 (2H, OCH_2), 1.82 m (2H, CH-CH), 1.12 m (2H, CH_2), 1.23 t (3H, CH_3), $J_{OCH_2-CH_3}$ = 7 Hz; mol wt. 140 (mass spectrometrically).

Diethyl Ester of Dicyclopropyl-2,2'-dicarboxylic Acid (IIc). A solution of 1 g (0.0088 mole) of EDA in 8 g of (Ic) was added dropwise to a mixture of 4.6 g of (Ic) and ∿ 0.5 g of anhydrous $CuSO_4$, heated to 110-120°C [total amount of (Ic) 5.4 g (0.0385 mole)]. The mixture was heated for 30 min at 110-120°C. By distillation, 1 g (50%) of (IIc), bp 110-115°C (3 mm) was isolated. Its IR and mass spectra were identical with those of the product obtained in the reaction of EDA with gaseous divinyl.

2-Vinylcyclopropanecarboxylic Acid (Ia). A 60-ml portion of ethanol and then 5.5 g (0.039 mole) of (IIc) were added to a saturated solution of 6 g (0.15 mole) of NaOH in water. The mixture was heated for 7 h at 60-70°C, and ethanol was evaporated in vacuo at 90°C (20 mm). The aqueous residue was washed with ether and neutralized with 10% H_2SO_4. The product was extracted with ether, and 3.4 g (80%) of a mixture of trans- and cis-(Ia) was isolated by distillation, bp 76-78°C (3 mm). IR spectrum (ν, cm^{-1}): 1640 (C=C), 1695 (C=O), 3000 (OH); PMR spectrum (in CCl_4, δ, ppm): 12 s (1H, OH), 4.9-6.2 (3H, $CH=CH_3$), 0.9-2.3 (4H, ring protons); mol. wt. 112 (mass spectrometrically).

2-(1,2-Dibromoethyl)cyclopropanecarboxylic Acid (Va) and Its Ethyl Ester (Vc). A solution of Br_2 in CH_2Cl_2 was added dropwise to a solution of 3.4 g (0.024 mole) of (Ic) cooled to – 50°C, or the catalyzate containing 80-95% of (Ic) in 10 ml of anhydrous CH_2Cl_2, until the bromine solution no longer decolorized. The mixture was evaporated, and the residue distilled. Thus, 7 g (95%) of (Vc), bp 106-109°C (3 mm) was obtained Similarly, (Va) was obtained from (Ia), mp 130.5-131.5°C (hexane – acetone). IR spectrum (KBr, ν, cm^{-1}): 600 (C–Br), 1710 (C=O), 3000 (OH); PMR spectrum [in a mixture of $(CF_3)_2CO$ + $CHCl_3$, δ, ppm)]: 9.43 s (1H, OH), 3.9 m (3M, $CHBrCH_2Br$), 0.9-2.0 m (4H, ring protons).

2-Ethynylcyclopropanecarboxylic Acid (IVa). A solution of 3.4 g (0.0113 mole) of (Vc) in 5 ml of ethanol was added for 70 min to a boiling solution of 8 g (0.14 mole) of KOH in 40 ml of 50% aqueous ethanol. The mixture was boiled for 25 min, and ethanol was distilled off. The residue was neutralized with 10% H_2SO_4, and 0.65 g (50%) of (IVa), bp 80-83°C (3 mm) was extracted with ether. IR spectrum (ν, cm^{-1}): 1710 (C=O), 2135 (C≡C), 3315 (≡C—H), 3000 (OH); PMR spectrum (in $CHCl_3$, δ, ppm): 11.5 s (OH), 1.75-2.05 m (3H, CHCHC≡CH), 1.0-1.6 m (2H, CH_2); mol. wt. 110 (mass spectrometrically).

Acid (IVa) was obtained similarly from (Va) in a yield of 33%.

Alkyl Esters of 2-Ethynylcyclopropanecarboxylic Acids (IVb) and (IVc). A 0.1 ml portion of concentrated H_2SO_4 was added to a solution of 0.4 g (0.0036 mole) of (IVa) in 2 ml of absolute alcohol. The mixture was boiled for 2.5 h, diluted with 1 ml of water, and extracted with ether (3 × 5 ml). The extracts were neutralized with a 5% solution of $NaHCO_3$, dried over anhydrous $MgSO_4$, and evaporated. Yield, 0.25 g (55%) of (IVc), bp 59-61°C (11 mm). IR spectrum (ν, cm^{-1}): 1725 (C = O), 2135 (C≡C), 3315 (≡C—H); PMR spectrum (in CCl_4, δ, ppm): 4.05 q (2H, OCH_2), 1.5-2.0 m (3H, CHCHC≡CH), 1.0-1.5 m (2H, CH_2), 1.18 t (3H, CH_3), $J_{OCH_2-CH_3}$ = 7 Hz; mol. wt. 138 (mass spectrometrically).

Compound (IVb) was obtained similarly, bp 64-68°C (20 mm). IR spectrum (ν, cm^{-1}) 1735 (C=O), 2130 (C≡C), 3315 (≡C—H); PMR spectrum (in CCl_4, δ, ppm): 3.64 s (3H, OCH_3), 1.5-2.0 m (3H, CHCHC≡CH), 1.0-1.5 m (2H, CH_2); mol. wt. 124 (mass spectrometrically).

Bis(2-carboxycyclopropyl)diacetylene (VIa). A mixture of 0.5 g (0.004 mole) of (IVa), 2.52 g of CuCl, 0.42 g of NH_4Cl, 12.5 ml of water, and 2.5 ml of ethanol was saturated with O_2 for 3.5 h with vigorous stirring. The mixture was diluted with 20 ml of 3 N HCl and extracted with ether. Yield 0.24 g (54%) of (VIa), mp 216-218°C (aqueous ethanol). IR spectrum (KBr, ν, cm^{-1}): 1705 (C=O), 2170 (C≡C), 3000 (OH); PMR spectrum (in CD_3OD, δ, ppm): 1.84 m (2H, CH—CH), 1.24 m (2H, CH_2); mol. wt. 218 (mass spectrometrically).

CONCLUSIONS

1. Thermocatalytic reaction of alkyl diazoacetates with an excess of gaseous divinyl at atmospheric pressure proceeds with the formation of the corresponding esters of isomeric 2-vinylcyclopropanecarboxylic acids with the trans-isomer predominating. The maximum yields (∿ 50%) are obtained when methyl diazoacetate is used with CuO as the catalyst.

2. A simple method for the preparation of 2-ethynylcyclopropanecarboxylic acid and its esters is proposed. It consists in the dehydrobromination with aqueous-alcoholic KOH of 2-(1,2-dibromoethyl)cyclopropanecarboxylic acid or its esters, obtained by the low-temperature bromination of 2-vinylcyclopropanecarboxylic acid or its esters.

3. By the oxidative dimerization of 2-ethynylcyclopropanecarboxylic acid, the previously unknown bis(2-carboxycyclopropyl)diacetylene was obtained.

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