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LETTERS TO THE EDITOR

Condensation of CH-Acids with *cis*-1,4-Dichlorobut-2-ene

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Abstract—Synthesis of tri- and five-membered carboxylates are discussed. Microwave irradiation has been shown to stimulate the condensation of CH-acids with allyl chlorides. The selectivity of formation of target products was depending on the CH-acid structure. Structures of the isolated compounds have been confirmed by ^{1}H and ^{13}C NMR spectroscopy and chromato–mass spectrometry data.

Keywords: CH-acid, allyl chloride, microwave irradiation, *gem*-disubstituted vinylcyclopropane, cyclopentenecarboxylate, C-alkylation

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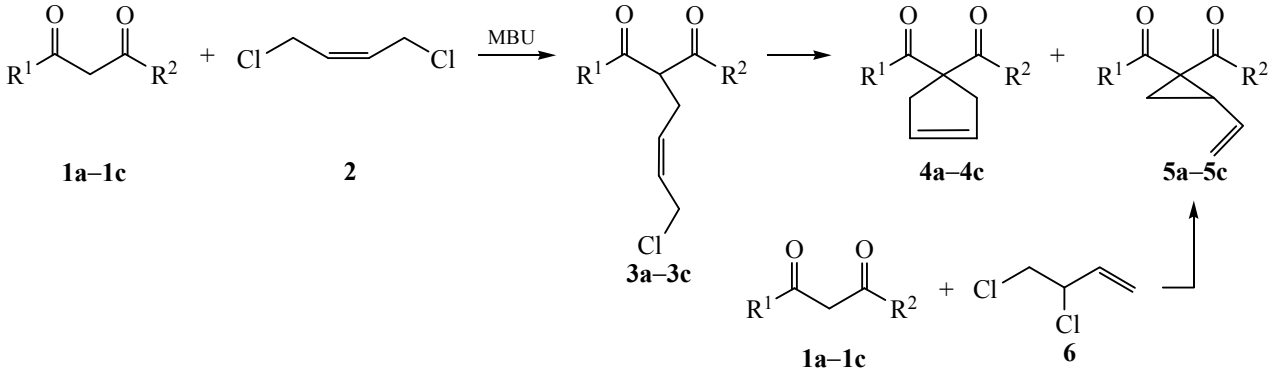
We have lately studied the alkylation of CH-acids with allyl chlorides and chloromethyl-*gem*-dichlorocyclopropanes, followed by the reduction of obtained malonates into polychlorinated cyclopropanecarboxylic acids [1, 2]. Extending these studies, we have shown [3] that diethyl malonate interacts with *cis*-1,4-dichlorobutene-2 in alkaline medium under the phase-transfer catalysis conditions to form mono- and *gem*-disubstituted malonates.

It is known that microwave irradiation can stimulate the reactions occurring under conditions of phase-transfer catalysis and affect the products structure [4]. We performed the reactions of pentane-2,4-dione **1a**, acetoacetic ester **1b**, and diethyl malonate **1c** with *cis*-1,4-dichlorobut-2-ene **2** under microwave irradiation (Scheme 1). The reactions afforded the target products **3a–3c** as well as their derivatives of the cyclopentane series **4a–4c** and *gem*-disubstituted vinylcyclopropanes **5a–5c**.

The microwave irradiation favored likely the elimination of chloride anion from compounds **3a–3c** giving the primary cation **A** that underwent reversible allyl rearrangement to afford the secondary cation **B**. The intramolecular attack of cations **A** and **B** at the polar C–H bonds resulted in the formation of cyclopentenes **4a–4c** and vinyl-*gem*-disubstituted cyclopropanes **5a–5c**, respectively (Scheme 2).

Compounds **5a–5c** were detected in the products of alkylation of CH-acids **1a–1c** with 2,3-dichlorobut-1-

Scheme 1.



$R^1 = R^2 = CH_3$ (**1a**); $R^1 = C_2H_5O$, $R^2 = CH_3$ (**1b**); $R^1 = R^2 = C_2H_5O$ (**1c**).

Selectivity of formation of compounds **4a**–**4c** and **5a**–**5c**[a]

CH-Acid	Conversion, %	Yield of the products, %	
1a	65	**4a** (12%)	**5a** (37%)
1b	75	**4b** (25%)	**5b**[b] (25%)
1c	90	**4c** (49%)	**5c** (21%)

[a] Molar ratio of **1** : **2** : K_2CO_3 = 0.1 : 0.15 : 0.1, acetonitrile as solvent, 10 wt % of e catalyst, microwave irradiation.
[b] Mixture of *cis* and *trans* isomers.

enes **6** by means of chromato–mass spectrometry which gave another confirmation of the suggested scheme of the three-membered ring formation.

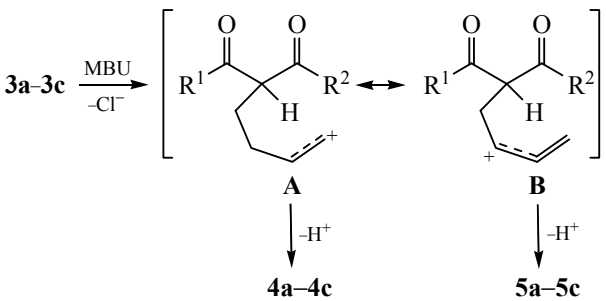
It should be noted that dichloride **2** reacts with malonic acid dinitrile in the presence of alkali metals alcoholates with exclusive formation of 2-vinyl-*gem*-dicyanocyclopropane [5], whereas the cyclopentane **4c** was the major product of the alkylation of diethyl malonate **1c** under similar conditions.

The selectivity of formation of three- (**5a**–**5c**) and five-membered (**4a**–**4c**) compounds was determined by the CH-acid structure (see table). The decrease in the CH-acid activity resulted in the increased region-selectivity of the formation of the cyclopropane fragment. Evidently, the slower interaction of cations **A** with CH-acid favored complete equilibration of the allyl rearrangement yielding cations **B**.

Physicochemical parameters of compounds **3c** and **4c** coincided with the reference data [3].

Synthesis of substituted carboxylates *(general procedure)*. A mixture of 0.1 mol of CH-acid **1**, 0.15 mol of 1,4-dichlorobut-2-ene **2** or 3,4-dichlorobut-1-ene **6**, 0.1 mol of K_2CO_3, 80 mL of anhydrous acetonitrile, and 10 wt% of triethylbenzylammonium chloride was stirred at 60°C during 6 h. In the case of microwave-assisted synthesis, the reaction duration was reduced to 1–2 h. After the reaction was complete the mixture was poured into water, extracted with methylene chloride, dried over Na_2SO_4, and evaporated. The residue was distilled in a vacuum or purified by chromatography of silica gel (**1c**, eluent: benzene–ethyl acetate, 8 : 2).

Scheme 2.



3-[(2*Z*)]-4-Chlorobut-2-enylpentane-2,4-dione (3a). Yield 2.2 g (12%), bp 132°C (5 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.25 s (6H, $\underline{CH_3}CO$), 2.40–2.45 m (2H, $\underline{CH_2}CH$), 4.10–4.15 m (1H, $\underline{CH}CH_2$), 4.60 d.d (2H, CH_2Cl, ^2J = 10.0, ^3J = 7.0), 5.30–5.60 m (2H, CH=CH). ^{13}C NMR spectra, δ_C, ppm: 26.37 ($\underline{CH}CH_2$), 26.39 ($\underline{CH_3}CO$), 37.68 (C), 73.16 ($\underline{CH}CH_2$), 127.92 (CH=CH), 205.06 (C=O). Mass spectrum, *m*/*e* (I_{rel}, %): 188 (1) $[M]^+$, 109 (10), 91 (5), 67 (7), 43 (100).

Ethyl (4*Z*)-2-acetyl-6-chlorohex-4-enoate (3b). Yield 5.5 g (25%), bp 151°C (5 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.20 s (3H, $\underline{CH_3}CO$), 1.95 s (3H, $\underline{CH_3}CH_2$), 2.60 d.d (1H, $\underline{CH_2}CH$, ^2J = 12.6, ^3J = 2.6), 2.90 d.d. (1H, $\underline{CH_2}CH$, ^2J = 12.6, ^3J = 2.6), 3.45–3.50 m (1H, $\underline{CH}CH_2$), 4.30 m (2H, $CH\underline{CH_2}$), 4.40 d (2H, CH_2Cl, ^2J = 8.5), 5.40–5.50 m (1H, $\underline{CH}$=CH), 5.80–5.90 m (1H, CH=$\underline{CH}$). ^{13}C NMR spectrum, δ_C, ppm: 13.96 ($\underline{CH_3}CO$), 23.05 ($\underline{CH_2}CH$), 29.67 ($\underline{CH_3}CH_2$), 38.43 (CH_2Cl), 59.41 ($\underline{CH}CH_2$), 61.43 ($CH_3\underline{CH_2}$), 129.55 (CH=CH), 170.37 (C=O), 202.73 (C=O). Mass spectrum, *m*/*e* (I_{rel}, %): 218 (1) $[M]^{+\cdot}$, 139 (100), 121 (5), 111 (35), 109 (25), 93 (35), 83 (5), 67 (55), 55 (5), 41 (100).

Cyclopent-3-enepentane-2,4-dione (4a). Yield 5.6 g (37%), bp 105°C (10 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.15 s (6H, $\underline{CH_3}CO$), 2.90 s (4H, $\underline{CH_2}CH$), 5.30 d.d (CH=CH, ^2J = 3.4, ^3J = 2.3). ^{13}C NMR spectrum, δ_C, ppm: 26.37 ($\underline{CH_3}CO$), 32.46 ($\underline{CH_2}CH$), 37.68 (C), 127.90 (CH=CH), 206.06 (C=O). Mass spectrum, *m*/*e* (I_{rel}, %): 152/0 (1) $[M]^{+\cdot}$, 109 (35), 67 (20), 43 (100), 39 (10).

Ethyl 1-acetylcyclopent-3-ene-1-carboxylate (4b). Yield 4.5 g (25%), bp 101°C (5 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.25 s (3H, $\underline{CH_3}CO$), 2.30 s (3H, $\underline{CH_3}CH_2$), 2.90 s (4H, $\underline{CH_2}CH$), 4.10–4.15 m (2H, $\underline{CH_2}CO$), 5.80 d.d (2H, CH=CH, ^2J = 3.5, ^3J = 1.6). ^{13}C NMR spectrum, δ_C, ppm: 14.07 ($\underline{CH_3}CO$), 26.92 ($\underline{CH_3}CH_2$), 33.47 ($\underline{CH_2}CH$), 62.28 ($\underline{CH_2}CO$), 63.38 (C), 132.79 (CH=CH), 202.49 (C=O). Mass spectrum, *m*/*e* (I_{rel}, %): 182 (1) $[M]^{+\cdot}$, 139 (35), 121 (35), 109 (9), 94 (25), 67 (55), 66 (33), 55 (5), 43 (100).

2-Vinylcyclopropylpentane-2,4-dione (5a). Yield 7.4 g (49%), bp 98°C (10 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.50 d.d (1H, $\underline{CH_2}CH$, ^2J = 8.8, ^3J =

7.3), 1.80 d.d (1H, $\underline{CH_2}CH$, ^2J = 8.8, ^3J = 7.3), 2.10 s (6H, $\underline{CH_3}CO$), 2.60–2.65 m (1H, $CH_2\underline{CH}$), 5.12–5.15 m (1H, $\underline{CH}=CH_2$), 5.27 m (2H, $CH=\underline{CH_2}$). ^{13}C NMR spectrum, δ_C, ppm: 20.27 ($\underline{CH_2}CH$), 26.92 ($\underline{CH_3}CO$), 30.84 ($CH_2\underline{CH}$), 37.69 (C), 118.90 ($CH=\underline{CH_2}$), 132.82 ($\underline{CH}=CH_2$), 202.49 (C=O). Mass spectrum, *m*/*e* (I_{rel}, %): 152 (1) $[M]^{+\cdot}$, 137 (5), 109 (20), 43 (100), 39 (10).

Ethyl 1-acetyl-2-vinylcyclopropanecarboxylate (5b). Yield 8.7 g (48%), bp 90°C (5 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.25 s (3H, $\underline{CH_3}CO$), 1.50 d.d (1H, $\underline{CH_2}CH$, ^2J = 4.6, ^3J = 1.1), 1.82 d.d (1H, $\underline{CH_2}CH$, ^2J = 4.6, ^3J = 1.1), 2.15 s (3H, $\underline{CH_3}CH_2$), 2.55–2.62 m (1H, $CH_2\underline{CH}$), 4.10 d (2H, $CH_3\underline{CH_2}$, ^2J = 1.0), 5.10 m (1H, $\underline{CH}=CH_2$), 5.25 m (2H, $CH=\underline{CH_2}$). ^{13}C NMR spectrum, δ_C, ppm: 14.20 ($\underline{CH_3}CH_2$), 20.09 ($\underline{CH_2}CH$), 25.90 ($CH_3\underline{CH_2}$), 30.53 (CH), 37.91 (C), 61.66 ($\underline{CH_3}CO$), 118.33 ($CH=\underline{CH_2}$), 132.79 ($\underline{CH}=CH_2$), 172.91 (C=O), 201.04 (C=O). Mass spectrum, *m*/*e* (I_{rel}, %): 182 (1) $[M]^{+\cdot}$, 139 (30), 121 (40), 109 (10), 94 (30), 66 (35), 43 (100), 39 (4).

Diethyl 2-vinylcyclopropane-1,1-dicarboxylate (5c). Yield 6.7 g (32%), bp 95°C (5 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 s (6H, $\underline{CH_3}CH_2$), 1.40 d.d (1H, $\underline{CH_2}CH$, ^2J = 4.7, ^3J = 2.1), 1.67 d.d (1H, $\underline{CH_2}CH$, ^2J = 3.9, ^3J = 2.6), 2.60–2.65 m (1H, $CH_2\underline{CH}$), 4.00–4.10 q (4H, $\underline{CH_2}CO$, *J* = 7.1), 4.98 d.d (1H, $CH=\underline{CH_2}$, ^2J = 17.0, ^3J = 10.4), 5.15 d.d (1H, $CH=\underline{CH_2}$, ^2J = 17.0, ^3J = 10.5), 5.45–5.50 m (1H, $\underline{CH}=CH_2$). ^{13}C NMR spectrum, δ_C, ppm: 14.01 ($\underline{CH_3}CH_2$), 20.34 ($\underline{CH_2}CO$), 30.98 ($\underline{CH}CH_2$), 36.35 (C), 118.20 ($CH=\underline{CH_2}$), 133.79 ($\underline{CH}=CH_2$), 167.28 (C=O). Mass spectrum, *m*/*e* (I_{rel}, %): 212 (1) $[M]^{+\cdot}$, 138 (40), 121 (80), 94 (70), 66 (100), 55 (30), 39 (60).

The chromatographic analysis of the products was performed using an HRGC 5300 Mega Series Carlo Erba chromatograph (flame ionization detector, 30 mL/min of helium flow as carrier gas, 25 m long column, temperature 50–280°C with a heating rate of 8 deg/min, detector temperature 250°C, evaporator temperature 300°C). Chromato–mass spectra were recorded using Fisons (quartz capillary column DB 560 50 m) and Focus instruments with a Finingan DSQII mass spectrometric detector (ion source temperature 200°C, injector temperature 50–270°C, heating at a rate 10 deg/min, a ThermoTR-5MS 50×2.5×10^{-4} m column, 0.7 mL/min of helium flow). Mass spectra were recorded under EI conditions. NMR spectra were recorded using a Bruker AVANCE-400 spectrometer (solutions in $CDCl_3$).

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