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LETTERS TO THE EDITOR

gem-Dichlorocyclopropanes Containing Acetylacetone Fragment in The Side Chain

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Previously we have described a method for preparation of substituted malonates and their derivatives by *C*-alkylating malonic ester with chloromethyl-*gem*-dichlorocyclopropanes [1, 2]. In continuation of these studies we performed the reactions of chloromethylcyclopropanes **1a**–**1c** with pentane-2,4-dione **2**.

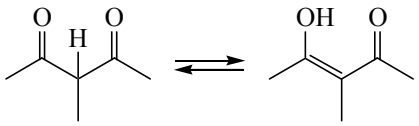
Chloromethyl derivatives **1a** and **1b** reacted with diketone **2** in the presence of sodium butoxide under microwave irradiation to form the corresponding monoadducts **3a** and **3b**. Compound **1c** was found to be inactive in this reaction (Scheme 1).

Reactivity of unsubstituted (**1a**) and substituted (**1b**) cyclopropanes in this reaction was virtually identical (see the table).

An alternative way to produce the desired substituted *gem*-dichlorocyclopropanes included *C*-alkylation of diketone **2** with chloroolefins **4a**–**4c** followed by dichlorocarbenation of unsaturated monoadducts **5a**–**5c** under phase-transfer catalysis as described in [1]. Thus, olefins **4a** and **4b** reacted to form the corresponding mono- (**5a**, **5b**) and bisadducts (**6a**, **6b**) (Scheme 2, table).

The bisadduct yields rose with increasing chloroolefin activity. Note that in the case of less active *trans*-1,3-dichloropropene **4c** the bisadduct was not formed.

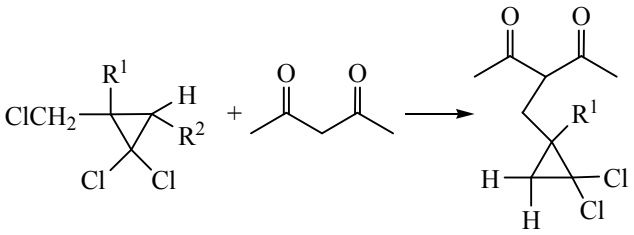
It should be noted that monosubstituted diketones **3a**, **3b**, **5a**–**5c** are in an equilibrium with enol forms in a ratio of 95 : 5 → 90 : 10, respectively. This was indicated by the integral signal intensity of hydroxyl (16.76 ppm) and CH proton (3.72 ppm) adjacent to two keto groups.



Practically quantitative output of carbenation of alkenylketones **5a**–**5c** makes it possible to consider a method of producing cyclopropane diketones **3a**–**3c** via intermediate alkylation of CH-acid **2** with the corresponding olefins **4a**–**4c** more efficient.

Olefin **5c** and cyclopropane **3c** which are derivatives of *trans*-1,3-dichloropropene **4c** retain the *trans*-configuration. This was indicated by the presence of the signals of the double bond protons in the NMR spectrum of compounds **5c** appeared at 5.80 and 6.06 ppm as doublets of triplets with ^3J = 13.3 Hz, whereas the analogous protons in *cis*-isomer resonated in a stronger field with the coupling constant ^3J = 7.3 Hz [3]. The NMR spectrum of compound **3c** had the signal of the proton at C^8 atom of the cyclopropane ring at 3.20 ppm as a doublet with a coupling constant

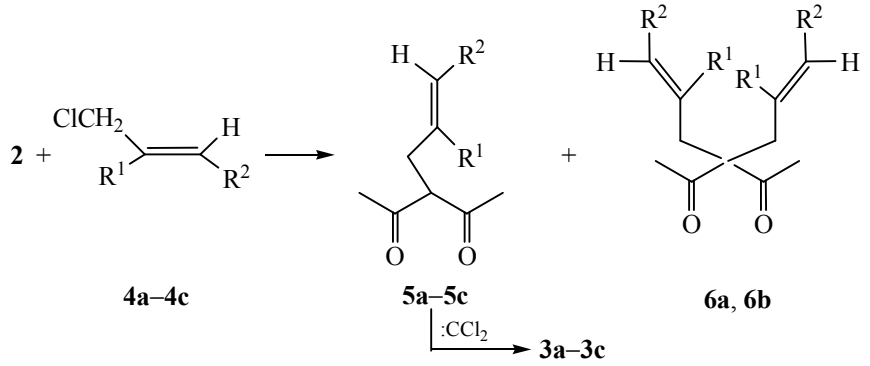
Scheme 1.



1a–1c **2** **3a**, **3b**

R^1 = H (**1a**, **3a**); CH_3 (**1b**, **3b**); R^2 = H (**1a**, **1b**, **3a**, **3b**); Cl (**1c**).

Scheme 2.



R^1 = H (**4a**, **4c**, **5a**, **5c**, **6a**, **6c**); CH_3 (**4b**, **5b**, **6b**); R^2 = H (**4a**, **4b**, **5a**, **5b**, **6a**, **6b**); Cl (**4c**, **5c**).

^3J = 6.2 Hz. The same proton signal in *cis*-isomer appeared in a weak field (3.57 ppm, ^3J = 8.0 Hz) [3].

Synthesis of dichlorocyclopropylacetylacetones (3a–3c). *a*. A mixture of 0.01 mol (1.0 g) of pentane-2,4-dione, 0.001 mol (0.1 g) of sodium butoxide, 0.01 g catamine AB, and 60 mL of anhydrous acetonitrile was under microwave irradiation at constant stirring for 30 min. The mixture was then cooled to room temperature and was charged with 0.015 mol of the corresponding dichlorocyclopropane **1**. Next, the mixture was irradiated with stirring for 4–6 h. After completion of the reaction (GLC monitoring), the resulting mixture was cooled to room temperature, washed with water, and extracted with chloroform. The organic layer was dried with potassium carbonate and evaporated. The residue was distilled in a vacuum.

b. A mixture of 0.01 mol of the corresponding ester **5**, 30 mL of chloroform, 32 g of a 50% solution of NaOH, and 0.001 mol (0.23 g) of triethylbenzylammonium chloride was stirred at 0–5°C for 6–9 h until complete conversion of the substrate. After the reaction was completed (GLC monitoring) the mixture was washed with water until neutral. The organic layer was dried with calcium chloride and evaporated. The residue was distilled in a vacuum.

3-[(2,2-Dichlorocyclopropyl)methyl]pentane-2,4-dione (3a). Yield 65% (*a*), 90% (*b*), bp 139°C (4 mmHg). ^{1}H NMR spectrum, δ, ppm: 0.90 m (1H, C^7H), 1.30–1.36 m (2H, C^8H_2) 1.60–1.65 m (2H, C^6H_2), 2.40 s (6H, C^1H_3, C^5H_3), 3.55–3.60 m (1H, C^3H). ^{13}C NMR spectrum, δ_C, ppm: 24.80 (C^7H), 27.11 (C^6H_2), 30.78 (C^1H_3, C^5H_3), 32.15(C^8H_2), 58.57 (C^3H, C^9Cl_2), 191.17 (C^2=O, C^4=O). Mass spectrum, *m*/*e* (I_{rel}, %): 143 (10), 130 (40), 109 (10), 111 (4), 113 (1), 95 (26), 43 (100).

3-[(2,2-Dichloro-1-methylcyclopropyl)methyl]-pentane-2,4-dione (3b). Yield 70% (*a*), 95% (*b*), bp 141°C (3 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.20 s (3H, $C^{10}H_3$), 1.60 d (2H, C^8H_2, ^2J = 7.5), 2.40 s (6H, C^1H_3, C^5H_3), 2.30–2.60 m (2H, C^6H_2), 3.55–3.60 m (1H, C^3H). ^{13}C NMR spectrum, δ_C, ppm: 18.19 ($C^{10}H_3$), 24.80 (C^1H_3, C^5H_3), 32.58 (C^6H_2, C^8H_2), 66.53 (C^3H, C^9Cl_2), 191.17 (C^2=O, C^4=O). Mass spectrum, *m*/*e* (I_{rel}, %): 144 (20), 123 (7), 109 (13), 43 (100).

3-[(2,2,3-Trichloro-1-methylcyclopropyl)methyl]-pentane-2,4-dione (3c). Yield 85% (*b*), bp 149°C (2 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.05–2.10 m (1H, C^7H), 2.30 s (6H, C^1H_3, C^5H_3), 2.70–2.80 m (2H, C^6H_2), 3.20 d (1H, C^8H, ^3J = 6.2), 4.30 d.d (1H, C^3H, ^3J = 7.5, ^2J = 9.5). ^{13}C NMR spectrum, δ_C, ppm: 24.79 (C^1H_3, C^5H_3), 30.85 (C^6H_2, C^7H), 40.39 (C^8H), 68.55 (C^3H, C^9Cl_2), 191.17 (C^2=O, C^4=O). Mass spectrum, *m*/*e* (I_{rel}, %): 131 (40), 133 (6), 135 (1), 97 (10), 43 (100).

Synthesis of compounds 5 and 6. A mixture of 0.01 mol (1.0 g) of pentane-2,4-dione, 0.001 mol

Alkylation of pentane-2,4-dione **2**[a]

Substrate (A)	Time, h	Adduct (yield, %)	
1a	4[b]	**3a** (65%)	
1b	4[b]	**3b** (70%)	
4a	2	**5a** (75%)	**6a** (10%)
4b	3	**5b** (80%)	**6b** (20%)
4c	1.5	**5c** (50%)	–

[a] Molar reagents ratio A : **2** : BuONa = 1.5 : 1 : 0.1, acetonitrile, microwave irradiation. [b] Catalyst catamine AB, 10 wt % relative to diketone **2**.

(0.1 g) of sodium butylate, and 60 mL of anhydrous acetonitrile was irradiated at constant stirring for 20 min. The mixture was then cooled to room temperature and was charged with 0.015 mol of the corresponding alkene **4**. Next, irradiation was continued for 2 h to complete conversion of pentane-2,4-dione. Upon completion of the reaction (GLC monitoring) the mixture was cooled to room temperature, washed with water, and extracted with chloroform. The organic layer was dried with potassium carbonate and evaporated. The residue was distilled in a vacuum.

2-Allylpentane-2,4-dione (5a). Yield 75%, bp 81°C (10 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.15 s (6H, C^1H_3, C^5H_3), 2.60 t (2H, C^6H_2, ^3J = 7.2), 3.70 t (1H, C^3H, ^3J = 7.0), 5.00–5.10 m (1H, C^8H), 5.55–5.65 m (1H, C^8H), 5.75–5.85 m (1H, C^7H). ^{13}C NMR spectrum, δ_C, ppm: 31.08 (C^1H_3, C^5H_3), 32.13 (C^6H_2), 67.90 (C^3H), 117.43 (C^8H_2), 134.02 (C^7H), 203.57 (C^2=O, C^4=O). Mass spectrum, *m*/*e* (I_{rel}, %): 140 (1) $[M]^+$, 98 (13), 97 (20), 83 (11), 43 (100).

3-(2-Methylprop-2-enyl)pentane-2,4-dione (5b). Yield 80%, bp 91°C (6 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.72 s (3H C^9H_3), 2.05 s (6H, C^1H_3, C^5H_3), 2.50 d (2H, C^6H_2, ^3J = 7.5), 3.88–3.92 m (1H, C^3H), 4.60–4.80 m (2H, C^8H_2). ^{13}C NMR spectrum, δ_C, ppm: 24.19 (C^9H_3), 27.04 (C^1H_3, C^5H_3), 38.24 (C^6H_2), 70.38 (C^3H), 114.30 (C^8H_2), 140.92 (C^7), 206.87 (C^2=O, C^4=O). Mass spectrum, *m*/*e* (I_{rel}, %): 112 (13), 97 (20), 85 (10), 43 (100).

3-(2*E*)-(3-Chloroprop-2-enyl)pentane-2,4-dione (5c). Yield 50%, bp 135°C (7 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.15–2.20 s (6H, C^1H_3, C^5H_3), 2.60 t (2H, C^6H_2, ^3J = 7.4), 3.70 t (1H, C^3H, ^3J = 7.2), 5.80 d.t (1H, C^7H, ^3J = 13.3, ^3J = 7.4), 6.06 t (1H, C^8H, ^3J = 13.3). ^{13}C NMR spectrum, δ_C, ppm: 22.87 (C^1H_3, C^5H_3), 28.79 (C^6H_2), 67.33 (C^3H), 120.11 (C^7H), 129.18 (C^8H), 202.75 (C^2=O, C^4=O). Mass spectrum, *m*/*e* (I_{rel}, %): 131 (38), 133 (12), 135 (4), 97 (15), 43 (100).

Diallylpentane-3,3-2,4-dione (6a). Yield 10%, bp 132°C (3 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.05 s (6H, C^1H_3, C^5H_3), 2.60 d (4H, C^6H_2, C^9H_2, ^3J = 7.3), 5.10 d.d (4H, C^7H, $C^{10}H$, ^3J = 9.5), 5.50–5.60 m (C^7H, $C^{10}H$). ^{13}C NMR spectrum, δ_C, ppm: 25.70 (C^1H_3, C^5H_3), 35.14 (C^6H_2, C^9H_2), 63.50 (C^3), 117.95 (C^7H, $C^{10}H$), 133.04 (C^8H, $C^{11}H$), 206.95 (C^2=O, C^4=O). Mass spectrum, *m*/*e* (I_{rel}, %): 138 (9), 123 (9), 97 (24), 79 (6), 43 (100).

3,3-Bis(2-methyl-2enyl)pentane-2,4-dione (6b). Yield 20%, bp 137°C (3 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.60 s (6H, C^9H_3, $C^{13}H_3$), 2.15 s (6H, C^1H_3, C^5H_3), 2.80 d (4H, C^6H_2, $C^{10}H_2$, ^2J = 2.0), 4.60–4.80 m (4H, C^8H_2, $C^{12}H_2$). ^{13}C NMR spectrum, δ_C, ppm: 24.15 (C^9H_3, $C^{13}H_3$), 27.01 (C^1H_3, C^5H_3), 38.24 (C^6H_2, $C^{10}H_2$), 70.38 (C^3), 114.00 (C^8H_2, $C^{12}H_2$), 140.92 (C^7, C^{11}), 206.81 (C^2=O, C^4=O). Mass spectrum, *m*/*e* (I_{rel}, %): 112 (17), 98 (20), 85 (45), 43 (100).

Chromatographic analysis of the reaction products was performed on a chromatograph HRGS 5300 Mega Series Carlo Erba equipped with a flame ionization detector (carrier gas helium, flow rate 30 mL/min, column length 25 m, ramp 50–280°C, heating rate 8 deg/min, detector temperature 250°C, evaporator temperature 300°C). GC-MS spectra were recorded on a Fisons (quartz capillary column DB 560, 50 m) and Focus instrument equipped with Finnigan DSQII mass spectrometric detector (ion source temperature 200°C, direct input temperature 50–270°C, heating rate 10 deg/min, column ThermoTR-5MS, $50 \times 2.5 \times 10^{-4}$ m, a helium flow rate 0.7 mL/min). Mass spectra were recorded in an electron impact ionization mode. NMR spectra were registered on a Bruker AVANCE-400 spectrometer in $CDCl_3$.

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