ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 1029–1032. © Pleiades Publishing, Ltd., 2009.
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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Relative Activity of Alkenyl-*gem*-Dichlorocyclopropanes in the Reactions of Hydrogenation and Alkylation

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Received November 6, 2008

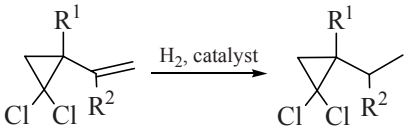
Abstract—Relative activity of alkenyl-*gem*-dichlorocyclopropanes in reactions of hydrogenation and acid-catalyzed alkylation of benzene and toluene was studied.

DOI: 10.1134/S1070427209060196

Alkenyl-*gem*-dichlorocyclopropanes are formed in high yield and selectivity at the addition of dichlorocarbene to industrial dienes, and they can be regarded as accessible intermediates for the organic synthesis [1–3].

Various pathways of functionalization of a double bond proceeding with the retention of the *gem*-dichloro-cyclopropane fragment have been described [4, 5]. A significant interest presents the behavior of these compounds in practically important processes of hydrogenation and alkylation.

The heterogeneous catalysts Pd/Al_2O_3 and Ni/TiO_2 widely used in the industry for the reduction of vegetable fats and oils [6, 7] were found to be applicable to a selectively hydrogenation of double bonds in alkenylcyclopropanes **Ia–Ic** without destruction of carbocycle and substitution of halogen:



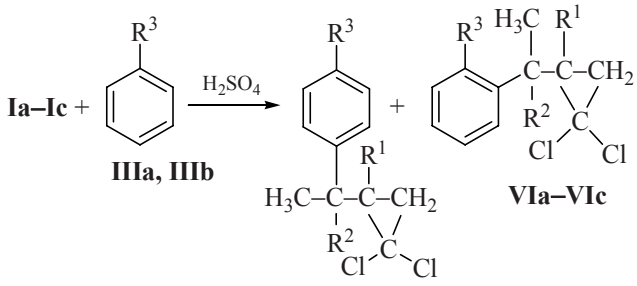
Ia–Ic **IIa–IIc**

$R^1 = R^2 = H$ (**Ia, IIa**); $R^1 = CH_3$, $R^2 = H$ (**Ib, IIb**); $R^1 = R^2 = CH_3$ (**Ic, IIc**).

Compounds with vinyl group **Ia** and **Ib** are close by the activity and are reduced both on Pd/Al_2O_3 and on Ni/TiO_2 practically completely in less than 3 h. Analogous result in the case of compound with isopropenyl group **Ic** is achieved in 4 h (Table 1).

The competitive hydrogenation of a mixture of compounds **Ia** and **Ic** at the conversion less than 30% showed that according to the yield of products **IIa** and **IIc** the vinyl derivative **Ia** is 3 times more active than the isopropenyl analog **Ic**.

In the presence of acid catalysts, olefin **Ib** is added to benzene [8]. It is shown that sulfuric acid alkylation (Table 2) of benzene (**IIIa**) and toluene (**IIIb**) by vinyl derivatives **Ia** and **Ib** proceeds with low yield (16–35%) of the corresponding substituted aromatic compounds **IVa**, **IVb** and **Va**, **Vb**, respectively:



$R^1 = R^2 = H$ (**Ia, IVa, Va**); $R^1 = CH_3$, $R^2 = H$ (**Ib, IVb, Vb, VIb**); $R^1 = R^2 = CH_3$ (**Ic, IVc, Vc, VIc**); $R^3 = H$ (**IIIa, IVa–IVc**); CH_3 (**IIIb, Va–Vc, Via–VIc**).

The yield of compounds **IVc**–**VIc**, the derivatives of olefin **Ic** is considerably higher (70–80%) that is characteristic for acid-catalyzed alkylation of aromatic compounds by isoalkenes [9].

Table 1. Hydrogenation of *gem*-dichlorocyclopropanes **Ia–Ic**. P = 6 atm, solvent octane, 60°C, olefin–catalyst ratio 10:1 (wt)

Compound	Catalyst	Reaction product	τ, h	Yield, %
Ia	Pd/Al_2O_3	**IIa**	30	30
			60	50
			150	93
Ib	Ni/TiO_2	**IIb**	30	32
			60	53
			150	95
	Pd/Al_2O_3		30	30
			60	48
			150	92
Ic	Pd/Al_2O_3	**IIc**	30	10
			60	25
			150	70
			240	90

Table 2. Alkylation of benzene **IIIa** and toluene **IIIb** by *gem*-dichlorocyclopropanes **Ia–Ic**. Benzene, toluene 0.073 mol, conc. H_2SO_4 0.0146 mol, olefin **Ia–Ic** 0.0146 mol, T = 40–45°C

Reagent	Reaction product	τ, h	Yield, % (*p/o* isomers ratio)
IIIa + **Ia**	**IVa**	14	10
IIIa + **Ib**	**IVb**	17	30
IIIa + **Ic**	**IVc**	9	73
IIIb + **Ia**	**Va** + **VIa**	7	12 (4:1)
IIIb + **Ib**	**Vb** + **VIb**	9	34 (4:1)
IIIb + **Ic**	**Vc** + **VIc**	4	82 (4:1)

Table 3. Relative activity of olefins **Ib–Id** in the reaction of benzene alkylation. Mole ratio olefin : C_6H_6 : H_2SO_4 = 1:5:1, T = 40–45°C, τ = 2 h

Reagent	Reaction product	Relative activity
IIIa + **Ib** + **Ic**	**IVb** + **IVc**	**IVc/IVb** = 3
IIIa + **Ib** + **Id**	**IVb** + **IVd**	**IVd/IVb** = 2.5

Note that under the studied conditions regardless the structure of alkenyl-*gem*-dichlorocyclopropane **Ia–Ic** the ratio of *ortho*- and *para*-isomers at the alkylation of toluene is constant and equals to 1:4.

Competitive alkylation of benzene by a mixture containing **Ib** and heptene-1 (**Id**) (2 h, the degree of conversion of olefins less than 30%) showed (Table 3), that according to the yield of compounds **IVb** and **IVd**, heptene-1 is 2.5 times more active than vinyl-*gem*-dichlorocyclopropane **Ib**. At the competitive alkylation of benzene by olefins **Ib** and **Ic** (2 h, conversion of olefins less than 30%) from the yields of products **IVb** and **IVc** follows that isopropenyl-*gem*-dichlorocyclopropane **Ic** is 4 times more active than the vinyl analog **Ia**. In all cases the formation of the products of alkylation was not accompanied by evolution of HCl and splitting of the cyclopropane fragment.

EXPERIMENTAL

The reaction products were analyzed on a Tsvet 50M chromatograph with the flame-ionization detector, carrier gas helium, flow rate 20 ml min^{-1}, column 1 m length, 3 mm diameter. As the stationary phase was used 5% SE-30 on Chromaton N-AW. The ^1H and ^{13}C NMR spectra were registered on a Tesla-BS-567 spectrometer (100 MHz), solvent $CDCl_3$, relative to TMS. Chromatomass-spectrometric analysis was carried out on a chromatomass-spectrometer HP-5859 coupled with a computer with mass-selective detector NR-5972a, the glass capillary column of 30 m length, 5% of phenylmethylsilicone on HP-5.

Alkenyl-*gem*-dichlorocyclopropanes **Ia–Ic** are synthesized employing a known procedure [2]. In the work were used unsaturated compounds of no less than 99% purity.

General procedure of hydrogenation of *gem*-dichlorocyclopropanes Ia–Ic. A metall 80 cm^3 reactor was charged with 0.01 mole of an appropriate olefin **Ia–Ic** and 0.2 g of catalyst (Pd/Al_2O_3 or Ni/TiO_2). The ratio olefin : catalyst = 10:1 (wt). As a solvent was used octane (40 ml). The reactor was closed hermetically and filled with hydrogen to the pressure 6 atm, the temperature in the reaction zone was 60°C. The regime of ideal mixing was reached by the automatic intensive shaking the reactor. To the end of experiment the reaction mass was filtered from the catalyst, the filtrate was dried over calcium chloride, the solvent was distilled off, and the product was isolated at the atmospheric pressure. The physicochemical characteristics of the synthesized compounds are presented in Table 4.

Alkylation by alkenyl-*gem*-dichlorocyclopropanes (Ia–Ic). To a mixture of 0.073 mol (5.7 g) of benzene

(or 6.7 g of toluene) and 0.0146 mole (1.43 g) of concentrated sulfuric acid at stirring and heating to 40–45°C was slowly added dropwise 0.0146 mol of the corresponding olefin (**Ia** 2.0 g, **Ib** 2.2 g, **Ic** 2.4 g). After the completion of addition the reaction mixture was heated for 4 to 17 h with vigorous stirring, then it was cooled and extracted with an appropriate solvent. Organic layer was washed with water, then with the solution of $NaHSO_3$, dried over $MgSO_4$, and the solvent was evaporated. The reaction products were separated by vacuum distillation.

The physicochemical characteristics of the synthesized compounds are listed in Table 4.

CONCLUSIONS

(1) Alkenyl-*gem*-dichlorocyclopropanes can be used successfully in the reactions of hydrogenation and alkylation.

(2) In the reactions of hydrogenation, vinyl-*gem*-dichlorocyclopropane is 3 times more active than

Table 4. Physicochemical characteristics of obtained products

Compound	bp, °C (*p*, mm Hg)	^{1}H NMR spectrum, δ, ppm	Mass-spectrum, *m/z* (I_{rel}, %)
1,1-Dichloro-2-ethylcyclopropane (**IIa**)	146	1.07–1.11 (t, 3H, H_3C); 1.41–1.58 (m, 2H, H_2C); 1.69–1.82 (d.t, 2H, CH_2CCl_2)	138, 140 (5) [M^+]; 123 (100); 110 (22); 75 (12); 87 (65); 51 (20); 39 (15)
1,1-Dichloro-2-methyl-2-ethylcyclopropane (**IIb**)	154	0.84–0.88 (t, 3H, H_3C); 1.21–1.30 (кв, 2H, H_2C); 1.24 (s, 2H, CH_2CCl_2); 1.33 (t, 3H, H_3C)	152, 154 (6) [M^+]; 123 (100); 110 (20); 75 (15); 87 (65); 51 (20); 39 (12)
1,1-Dichloro-2-methyl-2-isopropylcyclopropane (**IIc**)	170	0.92–0.95 (d, 3H, H_3C); 1.04–1.06 (d, 3H, H_3C); 1.07 (s, 3H, H_3C); 1.13–1.14 (d, 2H, CH_2CCl_2); 1.87–1.89 (m, 1H, HC)	166, 168 (5) [M^+]; 151 (3); 137 (18); 123 (100); 110 (22); 75 (12); 87 (65); 51 (20); 39 (15)
[1-(2,2-Dichlorocyclopropyl)ethyl]-benzene (**IVa**)	102 (2)	0.85–1.55 (m, 2H, CH_2CCl_2); 1.38) (d, 3H, H_3C); 1.70–1.84 (m, 1H, HC); 2.18–2.40 (m, 1H, HC); 7.18–7.39 (m, 5H, Ph)	216, 218 (1) [M^+]; 214 (14); 185 (53); 149 (100); 143 (10); 115 (30); 105 (6); 77 (7)
[1-(2,2-Dichloro-1-methylcyclopropyl]-benzene (**IVb**)	106 (2)	0.80–1.35 (m, 2H, CH_2CCl_2); 1.45) (d, 3H, H_3C); 1.78 (s, 3H, CH_3); 1.75–2.52 (m, 1H, HC); 7.00–7.18 (m, 5H, Ph)	228, 230 (1) [M^+]; 199 (13); 163 (46); 157 (10); 129 (10); 115 (10); 105 (100); 91 (17); 77 (16)
[1-(2,2-dichloro-1-methylcyclopropyl)-isopropyl]benzene (**IVc**)	117 (2)	1.21–1.23 (d, 3H, H_3C); 1.31 (s, 3H, H_3C); 1.37–1.57 (d, 2H, CH_2CCl_2); 1.41 (s, 3H, H_3C); 7.23–7.43 (m, 5H, Ph)	242, 244 (22) [M^+]; 207 (5); 191 (98); 155 (1); 129 (9); 105 (100); 91 (4); 77 (27)
Mixture of *p*- and *o*-isomers (4:1): [1-(2,2-Dichlorocyclopropyl)ethyl]-4-methylbenzene (**Va**) [1-(2,2-Dichlorocyclopropyl)ethyl]-2-methylbenzene (**VIa**)	118–119 (2)	*p*-Isomer **Va**: 1.32–1.34 (d, 3H, H_3C); 1.40–1.44 (m, 2H, CH_2CCl_2); 1.42–1.56 (m, 1H, $CHCCl_2$); 2.26 (s, 3H, H_3C–Ph); 7.06–7.10 (m, 4H, Ph)	*p*-Isomer **Va**: 228, 230 (5) [M^+]; 213 (4); 199 (55); 163 (100); 157 (10); 129 (20); 117 (5); 91 (5); 77 (10)

Table 4. (Contd.)

Compound	bp, °C (*p*, mm Hg)	^{1}H NMR spectrum, δ, ppm	Mass-spectrum, *m/z* (I_{rel}, %)
Mixture of *p*- and *o*-isomers (4:1): 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene (**Vb**) 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-2-methylbenzene (**VIb**)		*o*-Isomer **VIa**: 1.30–1.32 (d, 3H, H_3C); 1.38–1.42 (m, 2H, CH_2CCl_2); 1.40–1.55 (m, 1H, $CHCCl_2$); 2.19 (s, 3H, H_3C–Ph); 6.77–7.65 (m, 4H, Ph)	*o*-Isomer **VIa**: 228, 230 (5) [M^+]; 213 (4); 199 (23); 163 (75); 157 (6); 129 (8); 117 (1); 91 (2); 77 (4)
	121–122 (2)	*p*-Isomer **Vb**: 0.90–1.30 (m, 2H, - CH_2CCl_2); 1.39–1.40 (d, 3H, H_3C); 1.14 (s, 3H, H_3C); 2.25 (s, 3H, H_3C–Ph); 7.01–7.08 (m, 4H, Ph)	*p*-Isomer **Vb**: 242, 244 (12) [M^+]; 227 (1); 213 (43); 179 (37); 177 (100); 157 (8); 141 (19); 119 (55); 105 (13); 91 (100); 77 (10)
Mixture of *p*- and *o*-isomers (4:1): 1-[1-(2,2-dichloro-1-methylcyclopropyl)isopropyl]-4- methylbenzene (**Vc**) 1-[1-(2,2-dichloro-1-methylcyclopropyl)isopropyl]-2- methylbenzene (**VIc**)		*o*-Isomer **VIb**: 0.90–31.30 (m, 2H, CH_2CCl_2); 1.35–1.37 (d, 3H, H_3C); 1.14 (s, 3H, H_3C); 2.20 (s, 3H, H_3C–Ph); 6.84–7.62 (m, 4H, Ph)	*o*-Isomer **VIb**: 242, 244 (7) [M^+]; 227 (1); 213 (20); 179 (25); 177 (77); 157 (6); 141 (13); 119 (20); 105 (9); 91 (35); 77 (10)
	129–131 (2)	*p*-Isomer **Vc**: 0.88–1.40 (m, 2H, CH_2CCl_2); 1.22 (s, 3H, H_3C); 1.29 (s, 3H, H_3C); 1.40 (s, 3H, H_3C); 2.27 (s, 3H, H_3C–Ph); 6.89–6.91 (m, 4H, Ph)	*p*-Isomer **Vc** 256, 258 (3) [M^+]; 241 (23); 213 (2); 207 (4); 191 (98); 155 (2); 129 (10); 105 (100); 91 (5); 77 (25)
		o-Isomer **VIc**: 0.87–1.40 (m, 2H,) CH_2CCl_2); 1.21 (s, 3H, H_3C); 1.26 (s, 3H, H_3C); 1.38 (s, 3H, H_3C); 2.71 (s, 3H, H_3C–Ph); 6.81–7.53 (m, 4H, Ph)	*o*-Isomer **VIc** 256, 258 (3) [M^+]; 241 (13); 213 (1); 207 (2); 191 (43); 155 (2); 129 (6); 105 (100); 91 (5); 77 (20)

related isopropenyl derivative, while in acid-catalyzed alkylation of benzene and toluene isopropenyl-*gem*-dichlorocyclopropane is 4 times more active than vinyl analog.

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