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Alkylation of Benzene and Toluene with Chloromethyl-*gem*-dichlorocyclopropanes

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Abstract—By alkylation of benzene and toluene with chloromethyl-*gem*-dichlorocyclopropanes in the presence of $AlCl_3$, the corresponding 3,3-dichloroalkenyl derivatives have been obtained. It has been shown that methylation of the ring reduces the reactivity of substituted *gem*-dichlorocyclopropanes.

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Dichlorocarbenation of commercial dienes and chloroalkenes quantitatively yields the corresponding alkenyl- and chloroalkyl-*gem*-dichlorocyclopropanes, which are of particular interest as semiproducts in organic synthesis [1–3].

The use of vinyl-*gem*-dichlorocyclopropane in the alkylation of aromatic compounds was reported earlier [4, 5]. The resulting substituted benzenes and phenols are of considerable interest as additives for fuels, lubricating oils, and polymers [6]. It was also of interest to explore the possibility of their preparation by alkylation of aromatic hydrocarbons with chloromethyl-*gem*-dichlorocyclopropanes.

The present paper presents the results on alkylation of benzene and toluene with 2-chloromethyl-*gem*-dichlorocyclopropane (Ia) and 2-(chloromethyl)-2-methyl-*gem*-dichlorocyclopropane (Ib) in the presence of an aluminum chloride catalyst.

EXPERIMENTAL

The reagents 1,1-dichloro-2-chloromethylcyclopropane (Ia) and 1,1-dichloro-2-(chloromethyl)-2-methylcyclopropane (Ib) were synthesized according to the procedure described in [7]. A general procedure for the alkylation with chloromethyl-*gem*-dichlorocyclopropanes (Ia, Ib): to a stirred mixture of 0.05 mol (3.9 g) of benzene (or 4.6 g of toluene) and 0.0007 mol (0.09 g) of $AlCl_3$, 0.005 mol of *gem*-dichlorocyclopropane (0.8 g of Ia or 0.87 g of Ib)) was slowly added dropwise with stirring and heating to 70°C for 2 (in the case of Ia) or 3 h (in the case of Ib). After completion of the addition, the reaction mixture was further heated for 15 min with vigorous stirring and then poured into a beaker with ice and 10% hydrochloric acid and extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After solvent evaporation, the resulting residue was distilled in vacuum.

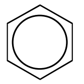
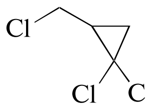
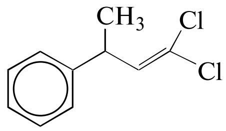
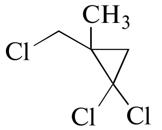
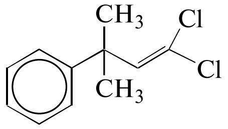
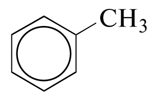
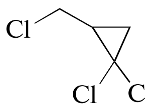
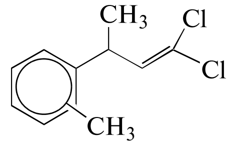
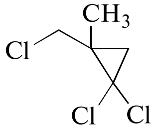
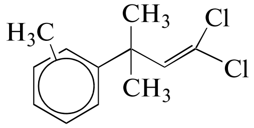
The reaction products were analyzed on an LKhM-8MD chromatograph equipped with a thermal conductivity detector and 2-m column with 5% SE-30 on a Chromaton N-AW support. The starting column temperature was 100°C, and the final one was 300°C, the programming rate was 20°C/min, the carrier gas (helium) flow rate was 30 mL/min, and the evaporator temperature was 250°C. The calculations were performed using the method of internal normalization, which is based on the reduction of a total area of peaks to 100%.

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz, respectively) in $CDCl_3$, using Me_4Si as an internal standard. Mass chromatograms were recorded on a SHIMADZU GCMS-QP2010 Plus instrument (EI, 70 eV, ion source temperature of 200°C, on-column injection temperature of 40–290°C, heating rate of 12°C/min).

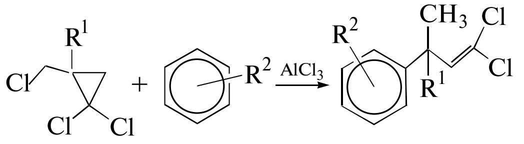
RESULTS AND DISCUSSION

The data obtained in this study (table) show that in the case of alkylation of benzene and toluene with reagents Ia and Ib in the presence of catalytic amounts of $AlCl_3$, the reaction is accompanied by opening of the cyclopropane ring and leads to the formation of the corresponding 3,3-dichloroalkenylderivatives IIa, IIb, and IIIa–IIId.

Alkylation of benzene and toluene by *gem*-dichlorocyclopropanes Ia and Ib

Reactants		Time, h	Products	Yield, %
	 Ia	2	 IIa	75
	 Ib	2	 IIb	21
	 Ia	3	 IIIa, b	70*
	 Ib	3	 IIIc, d	43**

* Mixture of *o*- and *p*-isomers (IIIa : IIIb = 1 : 7.5). **Mixture of *o*- and *p*-isomers (IIIc : IIId = 1 : 9).



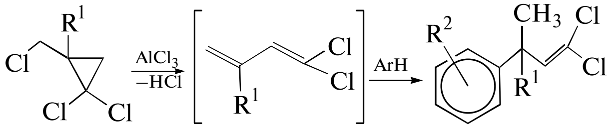
Ia, b IIa, b, IIIa–d

$R^1 = H$(Ia);
$R^1 = H$, $R^2 = H$(IIa);
$R^1 = H$, $R^2 =$ *ortho*-CH_3(IIIa);
$R^1 = H$, $R^2 =$ *para*-CH_3(IIIb);

$R^1 = CH_3$(Ib);
$R^1 = CH_3$, $R^2 = H$(IIb);
$R^1 = CH_3$, $R^2 =$ *ortho*-CH_3(IIIc);
$R^1 = CH_3$, $R^2 =$ *para*-CH_3(IIId).

In the case of chloromethyl derivative Ia, the yields of alkylation products are considerably higher than those with the use of chloride IIb. At the same time, in the reaction of Ia and IIb with toluene (table) yields the *o*- and *p*-isomers in approximately the same ratio (IIIa : IIIb = 1 : 7.5, IIIc : IIId = 1 : 9).

The formation of IIa, IIb, and IIIa–IIId is presumably due to the elimination of HCl molecule, involving cyclopropane ring opening by the C^1–C^2 bond and the formation of intermediate unstable diene which reacts with the aromatic substrate



This type of ring opening in substituted *gem*-dichlorocyclopropanes mediated by acid catalysts was described earlier in [8].

The relative activity of Ia and Ib toward benzene was estimated by means of competitive kinetics and it was found that the presence of methyl group in the cyclopropane moiety reduces the activity of compound Ib by a factor of 3, which is in a good agreement with our data (see table).

Individual substances IIa and IIb and a mixture of IIIa,b and IIIc,d isomers were isolated by vacuum distillation from the reaction mass of the interaction of the aromatic compounds with reagents Ia and Ib. Their structure and the *o*- to *p*-isomer ratio in the mixtures of IIIa,b and IIIc,d were determined by ^1H NMR and mass spectrometry.

(3,3-Dichloro-1-methylpropene-2-yl-1)benzene (IIa). Yield 75%, colorless liquid. Bp 96°C (5 mmHg). ^1H NMR ($CDCl_3$, δ, ppm): 1.36 (d, 3H, CH_3, ^3J 7.2 7.2 Hz), 3.75–3.86 (qu.d, 1H, CH_3–$\underline{CH}$, ^3J 7.2 Hz, ^3J 9.6 Hz), 5.93–5.96 (d, 1H, =CH, ^3J 9.6 Hz), 7.11–7.29 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, δ, ppm): 20.74 (CH_3), 40.31 (CH_3–$\underline{CH}$), 120.03 (CCl_2), 126.86 (*m*-Ar), 126.93 (*o*-Ar), 128.84 (*p*-Ar), 134.41 (=CH), 143.54 (Ph). Mass spectrum *m/e*, (I_{rel}, %):

200/202/204 M$^+$ (10/6/1.3), 185/187/189 $[\mathrm{M-CH_3^\bullet}]^+$ (5/3/0.8), 165/167 $[\mathrm{M-Cl^\bullet}]^+$ (18/6), 149/145 (60/20), 129 (100), 115 (23), 105 (12), 91 (4), 77 (30), 63 (20), 51 (37).

Mixture of 1-(3,3-dichloro-1-methylpropene-2-yl-1)-2-methylbenzene (IIIa) and 1-(3,3-dichloro-1-methylpropene-2-yl-1)-4-methylbenzene (IIIb) (ratio of isomers IIIa : IIIb = 1 : 7.5). Yield 70%, colorless liquid. Bp 112–114°C (5 mm Hg).

***o*-Isomer (IIIa).** ^{1}H NMR (CDCl$_3$, δ, ppm): 1.40 (d, 3H,CH$_3$, ^3J 6.9 Hz), 2.38 (s, 3H, $\underline{\mathrm{CH_3}}$–Ar), 3.97–4.07 (qu.d, 1H, CH$_3$–$\underline{\mathrm{CH}}$, ^3J 6.9 Hz, ^3J 9.3 Hz), 5.95–5.98 (d., 1H, =CH, ^3J 9.3 Hz), 7.10–7.21 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, δ, ppm): 20.34 ($\underline{\mathrm{CH_3}}$–Ar), 21.59 (CH$_3$), 31.98 (CH$_3$–$\underline{\mathrm{CH}}$), 123.15 (CCl$_2$), 123.89 (*p*-Ar), 125.60, 127.55 (*m*-Ar), 130.64 (*o*-Ar), 135.02 (*o*-Ar–CH$_3$), 137.02 (=CH), 139.42 (Ar). Mass spectrum *m/e*, (I_rel, %): 214/216/218 M$^+$ (28/18/3), 199/201/203 $[\mathrm{M-CH_3^\bullet}]^+$ (30/20/3.5), 179/181 $[\mathrm{M-Cl^\bullet}]^+$ (25/8), 163/165 (98/30), 143 (100), 128 (96), 119 (11), 115 (40), 91 (35), 77 (25), 63 (28), 51 (34).

***p*-Isomer (IIIa).** ^{1}H NMR (CDCl$_3$, δ, ppm): 1.41 (d, 3H, CH$_3$, ^3J 7.2 Hz), 2.35 (s, 3H, $\underline{\mathrm{CH_3}}$–Ar), 3.77-3.88 (qu.d, 1H, CH$_3$–$\underline{\mathrm{CH}}$, ^3J 7.2 Hz, ^3J 9.6 Hz), 5.97–6.0 (d, 1H, =CH, ^3J 9.6 Hz), 7.10–7.21 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, δ, ppm): 20.73 ($\underline{\mathrm{CH_3}}$–Ar), 21.10 (CH$_3$), 39.86 (CH$_3$–$\underline{\mathrm{CH}}$), 123.15 (CCl$_2$), 126.75 (*m*-Ar), 129.45 (*o*-Ar), 134.55 (=CH), 136.20 (*p*-Ar), 140.54 (Ar). Mass spectrum *m/e*, (I_rel, %): 214/216/218 M$^+$ (31/21/3), 199/201/203 $[\mathrm{M-CH_3^\bullet}]^+$ (40/25/4.5), 179/181 $[\mathrm{M-Cl^\bullet}]^+$ (35/12), 163/165 (95/30), 143 (100), 128 (97), 119 (18), 115 (28), 91 (30), 77 (23), 63 (22), 51 (28).

(3,3-Dichloro-1,1-dimethylpropene-2-yl-1)benzene (IIa). Yield 21%, colorless liquid. Bp 109°C (5 mmHg). ^{1}H NMR (CDCl$_3$, δ, ppm): 1.55 (s, 6H, $\underline{\mathrm{CH_3}}$–C–$\underline{\mathrm{CH_3}}$), 6.25 (s, 1H, =CH), 7.18–7.33 (m, 5H, Ar). ^{13}C NMR (CDCl$_3$, δ, ppm): 29.53 ($\underline{\mathrm{CH_3}}$–C–$\underline{\mathrm{CH_3}}$), 54.66 (CH$_3$–$\underline{\mathrm{C}}$–CH$_3$), 126.25 (*p*-Ar), 128.36 (*o*-Ar), 128.51 (*m*-Ar), 134.26 (CCl$_2$), 138.57 (=CH), 140.85 (Ar). Mass spectrum *m/e*, (I_rel, %): 214/216/218 M$^+$ (2), 199/201/203 $[\mathrm{M-CH_3^\bullet}]^+$ (1), 179/181 $[\mathrm{M-Cl^\bullet}]^+$ (45/15), 163/165 (18/6), 143 (100), 128 (68), 115 (11), 91 (15), 77 (17), 63 (12), 51 (20).

Mixture of 1-(3,3-dichloro-1,1-dimethylpropene-2-yl-1)-2-methylbenzene (IIIc) and 1-(3,3-dichloro-1,1-dimethylpropene-2-yl-1)-4-methylbenzene (IIId) (ratio of isomers IIIc : IIId = 1 : 9). Yield 43%, colorless liquid. Bp 122–124°C (5 mmHg).

***o*-Isomer (IIIc).** ^{1}H NMR (CDCl$_3$, δ, ppm): 1.54 (s, 6H, $\underline{\mathrm{CH_3}}$–C–$\underline{\mathrm{CH_3}}$), 2.37 (s, 3H, $\underline{\mathrm{CH_3}}$-Ar), 6.23(s, 1H, CH=), 7.01–7.26 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, δ, ppm): 21.14 ($\underline{\mathrm{CH_3}}$–Ar), 29.60 ($\underline{\mathrm{CH_3}}$–C–$\underline{\mathrm{CH_3}}$), 47.02 (CH$_3$–$\underline{\mathrm{C}}$–CH$_3$), 123.07 (*o*-Ar), 125.43 (*p*-Ar), 126.49, 128.28 (*m*-Ar), 134.43 (CCl$_2$), 135.73 (*o*-Ar–CH$_3$), 142.90 (=CH), 145.52 (Ar). Mass spectrum *m/e*, (I_rel, %): 228/230/232 M$^+$ (7/5/0.8), 213/215/217 $[\mathrm{M-CH_3^\bullet}]^+$ (1), 193/196 $[\mathrm{M-Cl^\bullet}]^+$ (50/18), 177/179 (22/7), 157 (100), 142 (60), 128 (20), 115 (27), 105 (11), 91 (18), 77 (17), 65 (18), 51 (12).

***p*-Isomer (IIId).** ^{1}H NMR (CDCl$_3$, δ, ppm): 1.53 (s, 6H, $\underline{\mathrm{CH_3}}$–C–$\underline{\mathrm{CH_3}}$), 2.35 (s., 3H, $\underline{\mathrm{CH_3}}$–Ar), 6.23 (s, 1H, CH=), 7.01–7.26 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, δ, ppm): 21.04 ($\underline{\mathrm{CH_3}}$–Ar), 29.60 ($\underline{\mathrm{CH_3}}$–C–$\underline{\mathrm{CH_3}}$), 49.13 (CH$_3$–$\underline{\mathrm{C}}$–CH$_3$), 125.86 (*o*-Ar), 129.07 (*m*-Ar), 134.43 (CCl$_2$), 135.42 (*p*-Ar–CH$_3$), 138.75 (=CH), 144.71 (Ar). Mass spectrum *m/e*, (I_rel, %): 228/230/232 M$^+$ (8/5/0.8), 213/215/217 $[\mathrm{M-CH_3^\bullet}]^+$ (1), 193/196 $[\mathrm{M-Cl^\bullet}]^+$ (55/18), 177/179 (29/10), 157 (100), 142 (64), 128 (23), 115 (28), 105 (11), 91 (18), 77 (18), 65 (17), 51 (12).

In ^{1}H NMR spectrum of IIa, IIb, and IIIa–IIId, the signals of cyclopropane ring protons in the region of 1.2–1.8 ppm disappear and new signals due to CH$_3$ protons and double bond protons appear at 1.4–1.5 and 5.9–6.5 ppm, respectively.

In the mass spectra of **IIa**, **IIb** and **IIIc**, **IIId**, the molecular ions have a low intensity to make 2 to 10%, whereas compounds **IIIa** and **IIIb** form stable molecular ions (m/z = 28–31%). The most abundant ions are those with m/z = 129 (for **IIa**), m/z = 143 (for **IIb**, **IIIa**, **IIIb**), and m/z= 157 (for **IIIc**, **IIId**) formed as a result of successive elimination of halogens. The main route of dissociation is almost the same for the *o*- and *p*-isomers of **IIIa–IIId**.

Thus, chloromethyl-*gem*-dichlorocyclopropanes can be successfully used as alkylation agents for preparation of substituted benzenes containing the dichloroalkenyl moiety.

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