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Alkylation of Aromatic Hydrocarbons with 2-Bromo-2-phenyl-*gem*-dichlorocyclopropane

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Abstract—The alkylation of aromatic hydrocarbons with 2-bromo-2-phenyl-*gem*-dichlorocyclopropane in the presence of catalytic quantities of aluminum chloride was found to afford the corresponding 2-aryl-3-phenyl-1,1-dichloroprop-1-enes. It was shown that the yield of the alkylation products depended on the nature of substituents in the aromatic ring. Compared with the thermal heating, microwave irradiation allows reducing the reaction time and increasing the yield of the corresponding 2-aryl-3-phenyl-1,1-di-chloroprop-1-enes, wherein the *ortho*-/*para*-isomers ratio changes.

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Substituted *gem*-dichlorocyclopropanes are widely used in organic synthesis [1]. We previously showed that the chloroalkyl-*gem*-dichlorocyclopropanes react with toluene and benzene to form the corresponding 3,3-dichloroalkenyl derivatives [2]. In continuation of this research we studied the alkylation of aromatic hydrocarbons **Ia**–**Id** with 2-bromo-2-phenyl-*gem*-dichlorocyclopropane **II**, which is readily formed from the available α-bromostyrene [3].

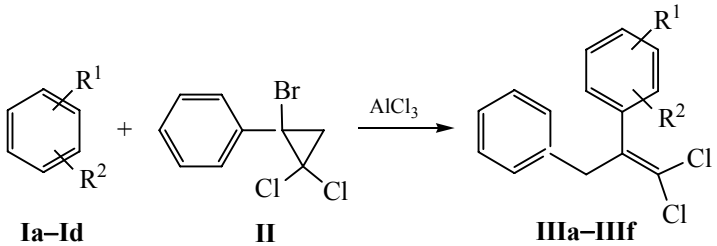
In the presence of the Friedel–Crafts reaction catalysts ($AlCl_3$) the alkylation of aromatic compounds **Ia**–**Id** with the bromo derivative **II** occurs through the cyclopropane ring opening to give the corresponding 2-aryl-3-phenyl-1,1-dichlorprop-1-enes **IIIa**–**IIIf**.

Methyl substituents in the aromatic ring of **Ib** and **Ic** reduce the activity of an aromatic compound; while the electronegative chlorine in **Id** has virtually no effect on the yield of alkylation products (see table).

Note that the microwave irradiation reduces the reaction time and increases almost two times the yield of alkylation products **IIIa**–**IIIf** . The selectivity of *o*-isomers formation increases in the case of compounds **Ib** and **Ic** (see table).

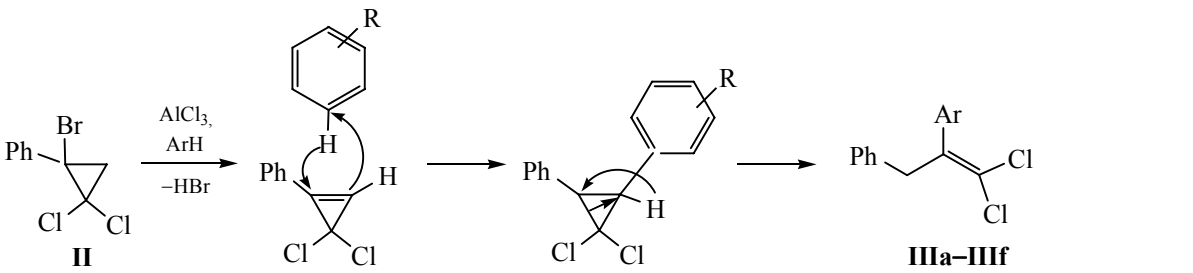
The formation of products **IIIa**–**IIIf** is probably due to the primary elimination of HBr molecule followed by alkylation of aromatic ring of **Ia**–**Id** with unstable cyclopropene that is accompanied by the ring opening and the migration of a hydrogen atom.

Earlier the rearrangement of the *gem*-dichlorocyclopropanes with the formation of 1,1-dichloroalk-1-enes has been described in [2, 4].



Ia–Id **II** **IIIa–IIIf**

$R^1 = R^2 = H$ (**Ia, IIIa**); $R^1 = H$, $R^2 = 2\text{-}CH_3$ (**Ib, IIIb**); $R^1 = H$, $R^2 = 4\text{-}CH_3$ (**IIIc**); $R^1 = R^2 = 2,4\text{-}CH_3$ (**Ic, IIId**); $R^1 = H$, $R^2 =$ 2-Cl (**Id, IIIe**); $R^1 = H$, $R^2 = 4\text{-}Cl$ (**Id, IIIf**).



The products of the reaction of aromatic compounds **Ia**–**Id** with reagent **II** were isolated by vacuum distillation as individual compounds (**IIIa**, **IIId**) or as mixtures of isomers (**IIIb** + **IIIc**, **IIIe** + **IIIf**). Their structure and the ratio of *ortho*- and *para*-isomers in the mixture were determined by the ^{1}H and ^{13}C NMR spectroscopy, GC-MS method.

A feature of the ^{13}C NMR spectra of compounds **IIIa**–**IIIf**, recorded in the modulation of the constant of C–H coupling made (JMOD), is the presence of a signal characteristic of the methylene carbon atoms [42.20 (**IIIa**), 41.89 (**IIIb**), 39.52 (**IIIc**), 39.41 (**IIId**), 41.76 (**IIIe**), 39.61 ppm (**IIIf**)] and a signal of quaternary carbon atom of CCl_2-group [118.83 (**IIIa**), 118.76 (**IIIb**, **IIIc**), 118.82 (**IIId**), 119.93 (**IIIe**), 119.27 ppm (**IIIf**)]. The ^{13}C NMR spectra of *para*-isomers contain the mutually equivalent signals of the carbon atoms of double intensity, whereas in the spectra of *ortho*-isomers with different substituents all the carbon atoms of the aromatic rings have different chemical shifts [5]. On this basis the signals of the aromatic carbons in the spectrum of mixtures (**IIIb** + **IIIc**) and (**IIIe** + **IIIf**) were assigned to the corresponding *ortho*- and *para*-isomers.

In the mass spectra of compounds **IIIa**–**IIIf** there are stable molecular ions (10–40%). The most intensive are ions with *m*/*z* 191 (**IIIa**), 205 (**IIIb**, **IIIc**), 219 (**IIId**), 225/227 (**IIId**, **IIIf**) formed by successive elimination of halogens. The main direction of dissociation for *ortho*- and *para*-isomers (**IIIb**, **IIIc**, **IIIe**, **IIIf**) is similar.

Thus, 2-bromo-2-phenyl-*gem*-dichlorocyclopropane can be advantageously used as an alkylating agent to produce 2-aryl-3-phenyl-*gem*-dichloropropenes.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra (JMOD mode) were recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz, respectively) in $CDCl_3$, internal reference TMS. The GC-MS spectra were registered on a Focus instrument equipped with a mass spectrometric detector Finingan DSQ II (ion source temperature 200°C, temperature of the direct input 50–270°C, heating rate 10 deg min^{-1}, column Thermo TR-5MS $50\times2.5\times10^{-4}$ m, helium flow rate 0.7 ml min^{-1}). GLC analysis was performed on a Crystal-2000M chromatograph with a thermal conductivity detector, carrier gas helium, flow rate 1.5 l h^{-1}, the column length 2 m, 5% SE-30 on Chromaton N-AW.

Dihalocarbenylation procedure. To a mixture of 0.1 mol of α-bromostyrene and 0.2 g of TEBAC in 300 ml of chloroform was added dropwise 320 g of a 50% solution of NaOH within 2 h under heating at 40°C and vigorous stirring. Then the mixture was stirred for 1 h at 40°C, washed with water, concentrated, and distilled in vacuum.

2-Bromo-2-phenyl-*gem*-dichlorocyclopropane (II). Yield 95%, colorless liquid, bp 125–127°C (4 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.06 d (1H, $C^{3}H_a$, ^{2}J 9.0), 2.09 d (1H, $C^{3}H_b$, ^{2}J 9.0), 7.17–7.39 m

Alkylation of aromatic hydrocarbons with 2-bromo-2-phenyl-*gem*-dichlorocyclopropane [(**Ia–Id**):**II**:$AlCl_3$ = 7.8:1:0.3, *T* = 100°C]

Comp. no.	Reaction products	Time, h	Yield, % (*ortho*:*para*)
Ia	**IIIa**	2	47
		0.5[a]	98
Ib	**IIIb** + **IIIc**	2	37 (1:1)
		0.5[a]	65 (2.5:1)
Ic	**IIId**	2	29
		0.5[a]	60
Id	**IIIe** + **IIIf**	2	48 (1:1)
		0.5[a]	97 (2:1)

[a] Microwave irradiation, 420 W.

(4H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 35.43 (C^3H_2), 43.01 (C^2Br), 62.88 (C^1Cl_2), 128.71 (C^2H, C^6H, Ph), 129.01 (C^4H, Ph), 129.28 (C^3H, C^5H, Ph), 138.87 (C^1). Mass spectrum, *m/z* ($I_{rel,}$ %): 264/266/268/270 (1) $[M]^+$, 192/194 (5/5), 185/186/188 (10/6/1) $[M - Br]^+$, 149/151 (100/30), 115 (47), 89 (28), 75 (18), 63 (22).

Alkylation of aromatic hydrocarbons Ia–Id with 2-bromo-2-phenyl-*gem*-dichlorocyclopropane (II) (*general procedure*)**.** To a mixture of 39 mmol of arene **Ia–Id** and 1.4 mmol of $AlCl_3$ under stirring and heating to 90°C was added dropwise a solution of 5 mmol of 2-bromo-2-phenyl-*gem*-dichlorocyclopropane **II** in 11 mmol of the corresponding aromatic compound over 2 h. After the addition was completed, the reaction mixture was heated with vigorous stirring for further 15 min and then poured into a mixture of ice and 10% hydrochloric acid solution, then extracted with diethyl ether. The organic layer was washed with water and dried over $MgSO_4$. After evaporation of the solvent the residue was distilled in vacuum.

Alkylation of aromatic hydrocarbons Ia–Id with 2-bromo-2-phenyl-*gem*-dichlorocyclopropane II under microwave irradiation (*general procedure*)**.** A mixture of 50 mmol of arene **Ia–Id**, 1.4 mmol of $AlCl_3$ and 5 mmol of 2-bromo-2-phenyl-*gem*-dichlorocyclopropane **II** was stirred under irradiation in a domestic microwave oven Sanyo EM-S1073W at 420 W for 30 min. Then the reaction mixture was poured into a mixture of ice and 10% hydrochloric acid solution and extracted with diethyl ether. The organic layer was washed with water and dried over $MgSO_4$. After evaporation of the solvent the residue was distilled in a vacuum.

1,1'-(1,1-Dichloroprop-1-ene-2,3-diyl)biphenyl (IIIa). Colorless liquid, bp 142°C (2 mm Hg). ^{1}H NMR spectrum, δ, ppm: 3.95 s (2H, C^3H_2), 7.05–7.30 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 42.30 (C^3H_2), 118.83 (C^1Cl_2), 126.58 (C^4H, Ph), 127.73 ($C^{4'}H$, Ph), 128.18 (C^3H, C^5H, Ph), 128.38, ($C^{3'}H$, $C^{5'}H$, Ph), 128.27 ($C^{2'}H$, $C^{6'}H$, Ph), 128.67 (C^2H, C^6H, Ph), 136.99 ($C^{1'}$, Ph), 138.63 (C^1, Ph), 139.05 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 262/264/266 (16/10/2) $[M]^+$, 227/229 (24/7) $[M - Cl]^+$, 191 (74), 165 (17), 149/151 (100/30), 136 (14), 115 (12), 91 (74), 65 (47), 51 (25).

A mixture of 1-(1-benzyl-2,2-dichlorovinyl)-2-methylbenzene (IIIb) and 1-(1-benzyl-2,2-dichlorovinyl)-4-methylbenzene (IIIb). Colorless liquid, bp 152–154°C (2 mm Hg). ***ortho*-IIIb**. ^{13}C NMR spectrum, δ_C, ppm: 19.48 (CH_3), 41.89 (C^1H_2, Bn), 118.76 (C^2Cl_2), 125.65 (C^4H, Bn), 130.09 (C^4H, C_6H_4), 126.58 (C^3H, C^5H, Bn), 128.53 (C^3H, C_6H_4), 128.41 (C^5H, C_6H_4), 129.07 (C^2H, C^6H, Bn), 125.92 (C^6H, C_6H_4), 136.86 (C^2, C_6H_4), 135.09 (C^1, C_6H_4), 136.02 (C^1, Bn), 138.75 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 276/278/281 (16/7/4) $[M]^+$, 241/243 (54/16) $[M - Cl]^+$, 205 (100), 191 (18), 178 (12), 163/165 (41/11), 149/151 (54/21), 136 (13), 128 (13), 105 (56), 101 (33), 89 (16), 77 (31), 65 (20), 63 (21), 53 (11), 51 (28). ***para*-IIIc**. ^{13}C NMR spectrum, δ_C, ppm: 20.97 (CH_3), 39.52 (C^1H_2, Bn), 118.76 (C^2Cl_2), 125.65 (C^4H, Bn), 126.58 (C^3H, C^5H, Bn), 128.08 (C^3H, C^5H, C_6H_4), 127.66 (C^2H, C^6H, C_6H_4), 128.29 (C^2H, C^6H, Bn), 137.54 (C^4, C_6H_4), 133.86 (C^1, C_6H_4), 136.38 (C^1, Bn), 140.06 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 276/278/281 (22/12/2) $[M]^+$, 241/243 (59/12) $[M - Cl]^+$, 205 (83), 191 (12), 189 (17), 178 (12), 163/165 (66/31), 149/151 (41/17), 136 (21), 127 (15), 105 (100), 101 (36), 89 (17), 77 (39), 65 (19), 63 (21), 53 (9), 51 (33).

2-(1-Benzyl-2,2-dichlorovinyl)-1,4-dimethylbenzene (IIId). Colorless liquid, bp 163°C (2 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 19.23, 21.18 (CH_3), 39.64 (C^1H_2, Bn), 118.82 (C^2Cl_2), 127.51 (C^4H, Bn), 127.87 (C^3H, C^5H, Bn), 129.85 (C^3H, C_6H_3), 130.09 (C^5H, C_6H_3), 128.35 (C^2H, C^6H, Bn), 130.27 (C^6H, C_6H_3), 135.15 (C^2, C_6H_3), 135.48 (C^4, C_6H_3), 133.44 (C^1, C_6H_3), 134.10 (C^1, Bn), 138.95 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 290/292/294 (16/10/2) $[M]^+$, 255/257 (69/22) $[M - Cl^{\bullet}]^+$, 219 (100), 203(23), 177/179 (45/17), 149/151 (51/18), 119 (86), 101 (32), 91 (59), 77 (36), 65 (12), 51 (19).

A mixture of 1-(1-benzyl-2,2-dichlorovinyl)-2-chlorobenzene (IIIe) and 1-(1-benzyl-2,2-dichlorovinyl)-4-chlorobenzene (IIIf). Colorless liquid, bp 165–167°C (2mm Hg). ***ortho*-IIIe**. ^{13}C NMR spectrum, δ_C, ppm: 41.76 (C^1H_2, Bn), 119.93 (C^2Cl_2), 126.79 (C^4H, Bn), 129.52 (C^4H, C_6H_4), 127.93, 128.44 (C^3H, C^5H, C_6H_4), 128.02 (C^3H, C^5H, Bn), 128.29 (C^2H, C^6H, Bn), 128.38 (C^6H, C_6H_4), 138.74 (C^2, C_6H_4), 132.51 (C^1, C_6H_4), 137.46 (C^1, Bn), 134.76 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 296/298/300/302 (45/36/12/2) $[M]^{+\bullet}$, 261/263/265 (44/23/4) $[M - Cl^{\bullet}]^+$, 225/227 (100/35), 183/185/187 (57/31/13), 149/151 (43/15), 136/138 (28/9), 125/127 (53/17), 95 (59), 90 (33), 75 (15), 63 (21), 51 (17). ***para*-IIIf**. ^{13}C NMR spectrum, δ_C, ppm: 39.61 (C^1H_2, Bn), 119.27 (C^2Cl_2), 126.79 (C^4H, Bn), 128.02 (C^3H, C^5H, Bn), 130.12 (C^3H, C^5H, C_6H_4), 128.29 (C^2H, C^6H, Bn), 128.65 (C^2H, C^6H, C_6H_4), 138.42 (C^4, C_6H_4), 134.28 (C^1,

C_6H_4), 135.63 (C^1, Bn), 138.24 (C^1). Mass spectrum, *m*/*z* (I_{rel}, %): 296/298/300/302 (45/36/12/2) $[M]^{+\bullet}$, 261/263/265 (44/23/4) $[M - Cl^{\bullet}]^+$, 225/227 (100/35), 183/185/187 (57/31/13), 149/151 (43/15), 136/138 (28/9), 125/127 (53/17), 95 (59), 90 (33), 75 (15), 63 (21), 51 (17).

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