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CHEMISTRY

Reactions of Substituted *gem*-Dichlorocyclopropanes with Mono- and Dihydroxybenzenes

A. N. Kazakova, A. A. Bogomazova, and S. S. Zlotskii

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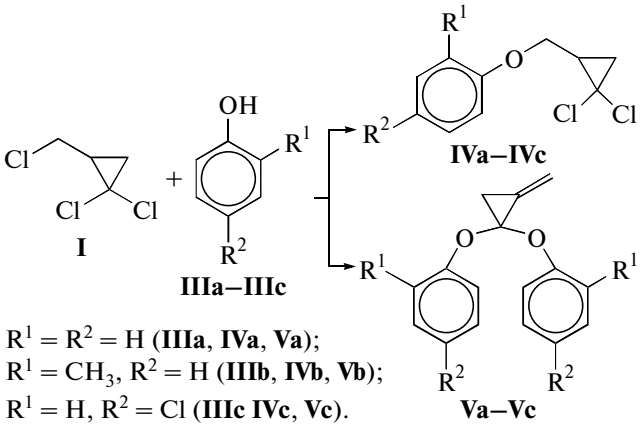
The reaction of *gem*-dibromocyclopropanes with phenols and alcohols is known to result in corresponding 1,1-diphenoxy- and dialkoxycyclopropanes [1]. It seems important to involve abundant and available (on the basis of commercial mono- and dichloropropenes) substituted *gem*-dichlorocyclopropanes in this reaction [2].

We have found conditions for the substitution for exocyclic and endocyclic chlorine atoms in 2-chloromethyl-*gem*-dichlorocyclopropane (**I**) and in *cis*- and *trans*-1,1,2-trichloro-3-chloromethylcyclopropanes (*cis*-**II**, *trans*-**II**) and accomplished this reaction.

Compound **I** reacts with phenols (**IIIa**–**IIIc**) under conditions of phase transfer catalysis to give competitively ethers (**IVa**–**IVc**) and ketals (**Va**–**Vc**).



$R^1 = R^2 = H$ (**IIIa**, **IVa**, **Va**);
$R^1 = CH_3$, $R^2 = H$ (**IIIb**, **IVb**, **Vb**);
$R^1 = H$, $R^2 = Cl$ (**IIIc IVc**, **Vc**).

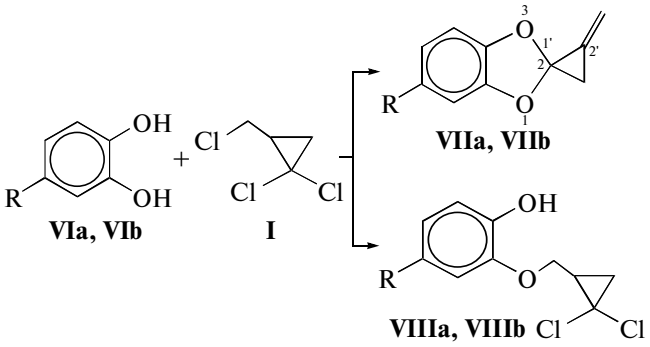
Scheme 1.

It is likely that only allyl chlorine atoms undergo substitution, therefore, ethers **IVa**–**IVc** do not react with phenols.

Ufa State Oil Technical University, ul. Kosmonavtov 1, Ufa, 450062 Bashkortostan, Russia

Ketals **Va**–**Vc** are the main products of thermal process, whereas the use of microwave radiation (MWR) sharply accelerates the substitution for the exocyclic chlorine atom, and ethers **IVa**–**IVc** form with high selectivity (Table 1).

Catechols **VIa** and **VIb** react with compound **I** to give 2'-methylenespiro[1,3-benzodioxolane-2,1'-cyclopropanes] (**VIIa**, **VIIb**) and ethers **VIIIa**, **VIIIb**.



R = H (**VIa**, **VIIa**, **VIIIa**); *tert*-C_4H_9 (**VIb**, **VIIb**, **VIIIb**).

Scheme 2.

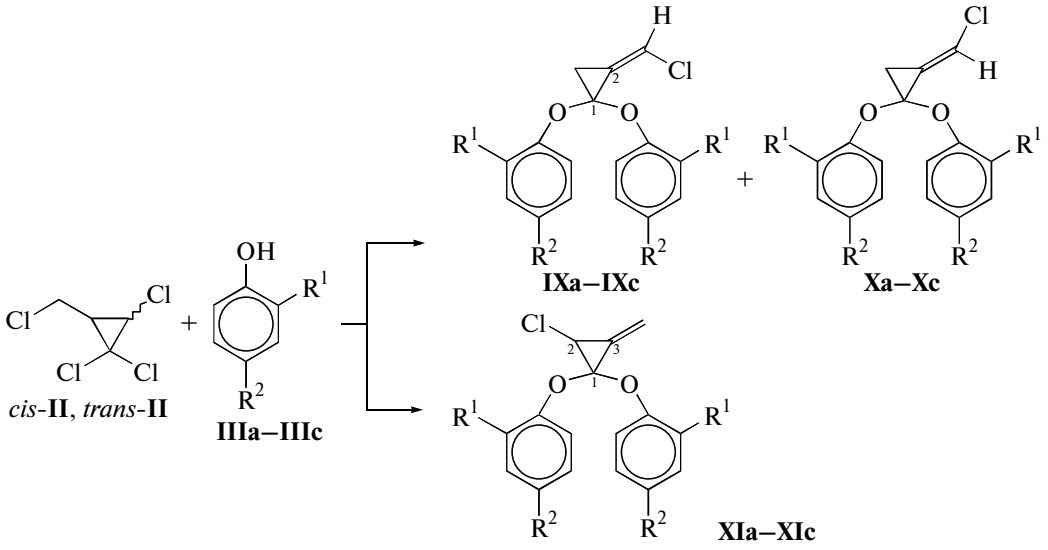
Exposure to microwave radiation sharply accelerates the displacement of chlorine atom in the CH_2Cl group of compound **I** and no ketals **VIIa**, **VIIb** form in this case (Table 2).

Table 1. Reaction of phenols **IIIa**–**IIIc** with 2-chloromethyl-*gem*-dichlorocyclopropane **I**

Phenol	Reaction products (yield, %)	
IIIa	**IVa** (5), (90)*	**Va** (86), (–)*
IIIb	**IVb** (20), (73)*	**Vb** (61), (–)*
IIIc	**IVc** (38), (77)*	**Vc** (59), (–)*

Note: Molar ratio NaOH : **IIIa**–**IIIc** : **I** : TEBAC = 6 : 3 : 1 : 0.02 (TEBAC, triethylbenzylammonium chloride) in 6.3 mL of DMSO, 60°C, 5 h. * MWR, 230 W, 1 h.

Phenols **IIIa**–**IIIc** react with *cis*- and *trans*-1,1,2-trichloro-3-chloromethylcyclopropanes (*cis*-**II**, *trans*-**II**) to give stereoisomeric chloromethylene (**IXa**–**IXc**, **Xa**–**Xc**) and methylene ketals (**XIa**–**XIc**).



$R^1 = R^2 = H$ (**IIIa**, **IXa**, **Xa**, **XIa**);
$R^1 = CH_3$, $R^2 = H$ (**IIIb**, **IXb**, **Xb**, **XIb**);
$R^1 = H$, $R^2 = Cl$ (**IIIc**, **IXc**, **Xc**, **XIc**).

Scheme 3.

The preferable reaction route is endocyclic dehydrochlorination, which leads, on account of migration of the double bond, to chloromethylene ketals (**IXa**–**IXc**, **Xa**–**Xc**) dominating in reaction mixture (Table 3).

Let us note that the use of microwave radiation in this reaction did not produce phenyl ethers.

EXPERIMENTAL

Initial 2-chloromethyl-*gem*-dichlorocyclopropane and *cis* and *trans*-1,1,2-trichloro-3-chloromethylcyclopropanes were obtained by the known procedure [2, 3]. Qualitative and quantitative analysis of the initial compounds and reaction products was performed with an LKhM-8MD chromatograph with thermal conductivity detection, helium as a carrier gas (column 2000 × 5 mm with 5% of SE-30). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (operating at 300.13 and 75.47 MHz, respectively) in $CDCl_3$ using Me_4Si as an internal reference. GC–MS analysis was carried out with a Focus

Table 2. Reaction of catechols **VIa**, **VIb** with 2-chloromethyl-*gem*-dichlorocyclopropane **I**

Catechol	Reaction products (yield, %)	
VIa	**VIIa** (41), (–)*	**VIIIa** (52), (62)*
VIb	**VIIb** (5), (–)*	**VIIIb** (45), (46)*

Note: Molar ratio NaOH : **VIa**, **VIb** : **I** : TEBAC = 4 : 2 : 1 : 0.02 in 3.8 mL of DMSO, 65–70°C, 2 h. * MWR, 230 W, 0.1 h.

Table 3. Reaction of *cis* and *trans*-1,1,2-trichloro-3-chloromethylcyclopropanes (*cis*-**II**, *trans*-**II**) with phenols **IIIa**–**IIIc**

Initial compounds	Yield of reaction products, % (isomer ratio)
cis-**II** + **IIIa**	**IXa**, **Xa**, **XIa**
	80 (10 : 1 : 2)
trans-**II** + **IIIa**	**IXa**, **Xa**, **XIa**
	90 (25 : 1 : 8)
cis-**II** + **IIIb**	**IXb**, **Xb**, **XIb**
	79 (11 : 2 : 1)
trans-**II** + **IIIb**	**IXb**, **Xb**, **XIb**
	87 (25 : 1 : 2)
cis-**II** + **IIIc**	**IXc**, **Xc**, **XIc**
	89 (16 : 1 : 4)
trans-**II** + **IIIc**	**IXc**, **Xc**, **XIc**
	94 (30 : 1 : 5)

Note: Molar ratio NaOH : **IIIa**–**IIIc** : *cis*-**II**, *trans*-**II** = 6 : 3 : 1 in 6.3 mL of DMSO, 0–5°C, 0.2 h.

instrument interfaced with a Finnigan DSQ II mass-spectral detector (EI, 70 eV, ionizing chamber temperature of 200°C, direct inlet temperature of 50–270°C, heating rate of 10 K/min).

General procedure for the synthesis of adducts **IVa–IVc, Va–Vc, VIIa, VIIb, VIIIa, VIIIb, IXa–IXc, Xa–Xc, XIa–XIc.**

A solution of 0.005 mol of substituted *gem*-dichlorocyclopropane (**I**, *cis*-**II**, or *trans*-**II**) in 1 mL of DMSO was added dropwise to a mixture of 0.015 mol of phenol **IIIa–IIIc** (or catechol **VIa–VIc**), 0.03 mol of NaOH (0.02 mol in the case of **VIa–VIc**), 0.0001 mol of TEBAC (in the case of compound **I**), 5.3 mL of DMSO (2.8 mL in the case of **VIa–VIc**) at 55–60°C (on cooling to 0–5°C in the case of compounds *cis*-**II**, *trans*-**II**) under vigorous stirring. After 2–5 h (0.2 h in the case of compounds *cis*-**I** and *trans*-**I**), the reaction mixture was diluted with water, extracted with chloroform, the organic layer was washed with 40 mL of 20% NaOH solution, then with water until neutral reaction, dried with freshly calcined $MgSO_4$, the chloroform was removed under a slight vacuum, and the residue was chromatographed on silica gel (hexane (cyclohexane) with ethyl acetate gradient from 5 to 100% as an eluent).

2'-Methylenespiro[1,3-benzodioxolane-2,1'cyclopropane] VIIa. Bp 79–81°C (4 mmHg).

^{1}H NMR ($CDCl_3$, δ, ppm): 2.14 (t, 2H, $C^{11}H_2$), 5.05 (s, 1H, $C^{12}H_2$), 5.33 (s, 1H, $C^{12}H_2$), 6.63–6.91 (m, 4H, C_6H_4).

MS (EI, 70 eV, *m/z* (I_{rel}, %)): 160 M^+ (81), 145 (37), 134 (100), 121 (3), 103 (4), 92 (7), 76 (6), 67 (18), 51 (14).

1,1-[(2*Z*)-2-(Chloromethylenecyclopropane-1,1-diyl)bis(oxydibenzene)] IXa. R_f 0.30 (hexane–AcOEt, 60 : 1, as eluent).

^{1}H NMR ($CDCl_3$, δ, ppm, *J,* Hz): 2.21 (d, 2H, cyclo-CH_2, *J* 3.23), 6.93 (t, 1H, CHCl, *J* 3.23), 7.05–7.37 (m, 10H, Ph).

^{13}C NMR ($CDCl_3$, δ, ppm): 21.34 (cyclo-CH_2), 85.3 (cyclo-C), 113.73 (=CHCl), 117.1 (*o*-Ph), 122.9 (*p*-Ph), 126.2 (cyclo-C=), 129.5 (*m*-Ph), 156.0 (Ph).

MS (*m/z* (I_{rel}, %)): 271/273 $[M-1]^+$ (1), 235 (2), 179/181 $[M-OPh]^+$ (39/14), 151/153 (34/11), 143 (19), 115 (100), 94 (17), 91 (56), 77 (78), 65 (21), 51 (51).

1,1-[(2*E*)-2-(Chloromethylenecyclopropane-1,1-diyl)bis(oxydibenzene)] Xa. R_f 0.21 (hexane–AcOEt, 60 : 1, as eluent).

^{1}H NMR ($CDCl_3$, δ, ppm): 2.13 (d, 2H, cyclo-CH_2, *J* 2.47), 6.37 (t, 1H, CHCl, *J* 2.6), 7.05–7.37 (m, 10H, Ph).

^{13}C NMR ($CDCl_3$, δ, ppm): 20.49 (cyclo-CH_2), 84.61 (cyclo-C), 115.34 (=CHCl), 117.1 (*o*-Ph), 122.9 (*p*-Ph), 125.99 (cyclo-C=), 129.5 (*m*-Ph), 156.0 (Ph).

MS (*m/z* (I_{rel}, %)): 271/273 M–1 (1), 235 (2), 179/181 M–OPh (42/13), 151/153 (32/10), 143 (19), 115 (100), 94 (15), 91 (45), 77 (75), 65 (17), 51 (39).

1,1-[2-Chloro-3-methylenecyclopropane-1,1-diyl)bis(oxydibenzene)] XIa. R_f 0.26 (hexane–AcOEt, 60 : 1, as eluent).

^{1}H NMR ($CDCl_3$, δ, ppm): 4.03 (t, 1H, cyclo-CHCl, *J* 2.07), 5.95 (d, 1H, $=CH_2$, *J* 1.55), 6.07 (d, 1H, $=CH_2$, *J* 1.03), 7.11–7.38 (m, 10H, Ph).

^{13}C NMR ($CDCl_3$, δ, ppm): 36.20 (cyclo-CHCl), 82.69 (cyclo-C–$(O-)_2$), 113.32 ($=CH_2$), 116.92, 117.29 (*o*-Ph), 122.95, 123.10 (*p*-Ph), 129.52, 129.72 (*m*-Ph), 132.30 (cyclo-C), 155.13, 156.11 (Ph).

MS (*m/z* (I_{rel}, %)): 272/274 $[M]^+$ (<0.1), 236 (<1), 207 (1), 179/181 $[M-OPh]^+$ (1/0.3), 161 (100), 131 (1), 121 (5), 94 (5), 77 (28), 65 (14), 51 (8).

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