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Alkylation of Phenols with Alkenyl-*gem*-Dichlorocyclopropanes

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Abstract—The alkylation of phenol and 2,6-di-*tert*-butylphenol with alkenyl-*gem*-dichlorocyclopropanes in the presence of boron trifluoride etherate was studied. The products were obtained with a yield of 45–50% of the theoretical value. The structure of the products was determined by spectral methods.

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The dichlorocarbenylation of industrial diene hydrocarbons leads to the formation of the corresponding alkenyl-*gem*-dihalocyclopropanes with quantitative yields, which are of interest as monomers and intermediary petrochemicals [1–3]. In particular, these olefins are successfully used for the production of polyfunctional compounds containing a *gem*-dihalocyclopropyl fragment [4, 5]. Alkyl- and aryl-*gem*-dichlorocyclopropanes demonstrate herbicidal and growth-stimulating activity and are of certain interest as promising plant protection chemicals [6].

In this work, we report the results of phenol alkylation with the products of butadiene (**Ia**) and isoprene (**Ib**) dichlorocarbenylation in the presence of boron trifluoride etherate.

EXPERIMENTAL

Alkenyl-*gem*-dichlorocyclopropanes were synthesized by the following method: a four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a dropping funnel was loaded with 0.1 mol of the corresponding olefin (butadiene or isoprene), 300 ml of chloroform, and 0.1 g (0.0004 mol) of the phase-transfer catalyst triethylbenzylammonium chloride. A solution of sodium hydroxide (320 g of a 50% solution) was dropped into the resultant mixture for 2 h under agitating stirring at room temperature or at –10°C in the case of isoprene and butadiene, respectively. The resultant mixture was additionally stirred for 1 h. The mixture was washed with water to pH 7. The lower organic layer was separated, dried with calcium chloride, and filtered off; after the evaporation of chloroform, the products of dichlorocarbenylation were isolated by atmospheric distillation.

The unsaturated compounds used were of at least 99% purity, reagent grade phenol was freshly distilled before the experiment, and 2,6-di-*tert*-butylphenol had a purity of 99.8%.

The procedure for the alkylation of phenols with alkenyl-*gem*-dichlorocyclopropanes **Ia** and **Ib** was as follows: the corresponding gem-dichlorocyclopropane (0.0146 mol) (of 2.0 g **Ia** or 2.2 g of **Ib**) was slowly added dropwise to a mixture of 0.073 mol (6.9 g) of phenol (or 15 g of 2,6-di-*tert*-butylphenol) and 0.01 mol (1.37 g) of the catalyst boron trifluoride etherate with stirring at a temperature of 50–60°C. The olefin : phenol : catalyst molar ratio was 1 : 5 : 1. The resulting mixture was additionally heated for 9–17 h with vigorous stirring, then cooled, and extracted by the corresponding solvent. The organic layer was washed with water and a $NaHCO_3$ solution and dried over $MgSO_4$. After the evaporation of the solvent, the products were isolated chromatographically on a column packed with silica gel (the eluent was a 19 : 5 hexane–ethyl acetate blend).

The GLC analysis was carried out on a Chrom-5 chromatograph with a flame-ionization detector and a 2-m column packed with Chromaton N-AW-DMC coated with a 5% SE-30 methylsiloxane elastomer with temperature programming from 50 to 280°C at a rate of 20°C/min; the carrier gas (helium) flow rate was 30 ml/min. The evaporator temperature was 300°C. The calculations were carried out using the method of internal normalization based on the reduction of the sum of peak areas to 100%.

The NMR spectra were recorded on a Tesla-BS-567 (100 Hz) spectrometer using tetramethylsiloxane as a standard. Gas chromatographic–mass spectrometric analysis was carried out on a computerized HP-5859 gas chromatograph–mass spectrometer equipped with an HP-5972A mass-selective detector and an HP-5 30-m glass capillary column coated with 5% phenyl methyl silicone.

RESULTS AND DISCUSSION

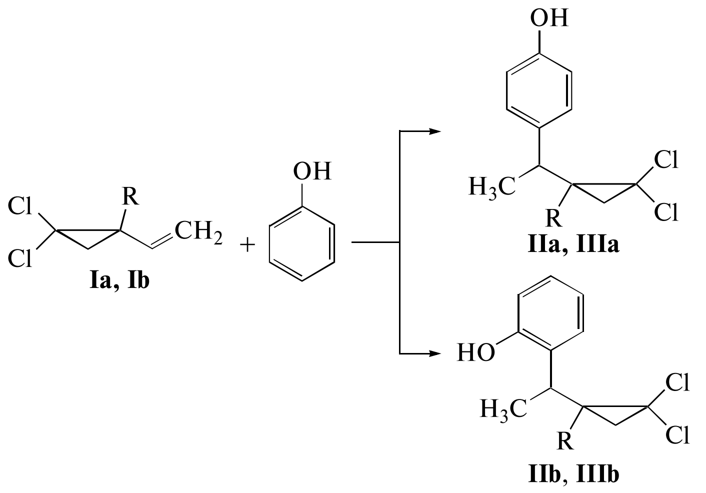
The obtained results show that in the presence of boron trifluoride etherate $BF_3O(C_2H_5)_2$, compounds

Table 1. Alkylation of phenol and 2,6-di-*tert*-butylphenol with *gem*-dichlorocyclopropanes Ia and Ib

Reactants		Products	Time (h)	Yield, % (*p*- : *o*-isomers)
Phenol	Ia	*p*-, *o*-Isomer mixture (1.2 : 1) IIa + IIb	17	43
	Ib	*p*-, *o*-Isomer mixture (1.2 : 1) IIIa + IIIb	15	45
2,6-Di-*tert*-butylphenol	Ia	IVa*	11	42
	Ib	IVb*	9	48

* About 5% of *o*-*tert*-butylphenol was found.

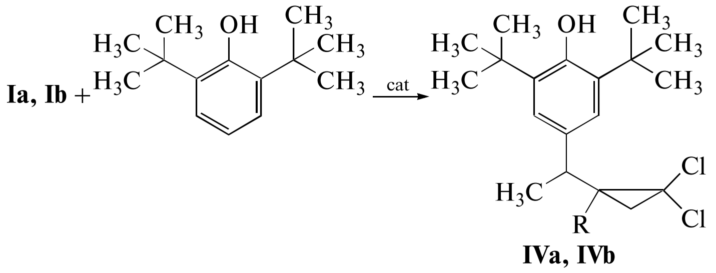
Ia and **Ib** alkylate phenol yielding a mixture of *o*- and *p*-isomers **IIa**, **IIb** and **IIIa**, **IIIb** in a ratio that slightly depends on the olefin structure (**IIa/IIb** ≈ **IIIa/IIIb** ≈ 1.3 : 1).



where R = H for **Ia**, **IIa**, and **IIb** or R = CH_3 for **Ib**, **IIIa**, and **IIIb**.

Yields close to 50% were reached within 15–20 h of the reaction (Table 1).

Similar values were obtained for the yields of products **IVa** and **IVb** in the alkylation of 2,6-di-*tert*-butylphenol with compounds Ia and Ib within 9–11 h of the experiment:



where R = H (**IVa**) or CH_3 (**IVb**).

It is obvious that the partial dealkylation of the initial 2,6-di-*tert*-butylphenol takes place under these conditions, as indicated by the appearance of *o*-*tert*-butylphenol (about 5%) in the resultant mixture. Using the method of concurrent kinetics, we evaluated the relative activity of compound**s Ia and Ib** as compared to 2,6-di-*tert*-butylphenol and found that the isoprene derivative is 1.3–1.5 times more active; this is in agreement with the obtained results (Table 1). The synthesized compounds were identified by proton NMR spectroscopy, mass spectrometry (Table 2), and elemental analysis.

Identification of the products by elemental analysis:

A mixture of *p*- and *o*-isomers (1.2 : 1): 4-[1-(2,2-(dichlorocyclopropyl)ethyl]phenol (**IIa**), 2-[1-(2,2-(dichlorocyclopropyl)ethyl]phenol (**IIb**):

Table 2. Physicochemical characteristics of the obtained compounds

Compound	^{1}H NMR spectrum, δ, ppm	mass spectrum, m/z (I_{rel}, %)*
p : o-isomer mixture(1.2 : 1) 4-[1-(2,2-(dichlorocyclopropyl)ethyl]phenol (**IIa**) 2-[1-(2,2-(dichlorocyclopropyl)ethyl]phenol (**IIb**)	p-isomer (**IIa**): 1.76–1.81 (m, $CHCCCl_2$);1.42–1.49 (dd, CH_2CCCl_2); 2.02–2.07 (m, CH); 1.34–1.41 (d, CH_3); 6.04 (s, OH-Ph); 6.61–7.39 (4H, Ph) o-isomer (**IIb**): 1.81–1.98 (m, $CHCCCl_2$);1.41–1.47 (dd, CH_2CCCl_2); 2.20–2.32 (m, CH); 1.42–1.43 (d, CH_3); 6.05 (s, OH-Ph); 6.71–7.14 (4H, Ph)	p-isomer (**IIa**): 230 (5) [M^+]; 150 (4); 121 (100); 109 (15); 94 (15); 77 (10); 51 (5) o-isomer (**IIb**): 230 (25) [M^+]; 150 (25); 121 (100); 109 (20); 94 (50); 77 (25); 51 (10)
p : o-isomer mixture(1.2 : 1) 4-[1-(2,2-(dichloro-1-methylcyclopropyl)ethyl]phenol (**IIIa**) 2-[1-(2,2-(dichloro-1-methylcyclopropyl)ethyl]phenol (**IIIb**)	p-isomer (**IIIa**): 1.32–1.39 (dd, CH_2CCCl_2); 1.90–1.95 (m, CH); 1.39–1.40 (d, CH_3); 1.15 (s, CH_3); 6.04 (s, OH-Ph); 6.61–7.09 (4H, Ph) o-isomer (**IIIb**): 1.30–1.36 (dd, CH_2CCCl_2); 2.24–2.27 (m, CH); 1.40–1.43 (d, CH_3); 1.15 (s, CH_3); 6.04 (s, OH-Ph); 6.61–7.09 (4H, Ph)	p-isomer (**IIIa**): 244 (44) [M^+]; 229 (85); 150 (25); 121 (100); 109 (10); 94 (25); 77 (60); 51 (20) o-isomer (**IIIb**): 244 (3) [M^+]; 229 (25); 150 (25); 121 (100); 109 (20); 94 (45); 77 (30); 51 (20)
2,6-Di-*tert*-butyl-4-[1-(2,2-(dichlorocyclopropyl)ethyl]phenol (**IVa**)	1.78–1.83 (dd, $CHCCCl_2$); 1.38–1.49 (m, CH_2CCCl_2); 1.78–1.79 (m, CH); 1.55–1.59 (d, CH_3); 5.37 (s, OH-Ph); 1.40 (s, t-Bu-CH_3); 6.77–7.00 (dd, 2H, Ph)	342 (5) [M^+]; 233 (10); 191 (30); 109 (20); 91 (20); 79 (30); 57 (100); 41 (10)
2,6-Di-*tert*-butyl-4-[1-(2,2-(dichloro-1-methylcyclopropyl)ethyl]phenol (**IVb**)	1.36–1.39 (m, CH_2CCCl_2); 1.69–1.79 (m, CH); 1.45–1.51 (d, CH_3); 1.65 (s, CH_3; 5.37 (s, OH-Ph); 1.40 (s, t-Bu-CH_3); 6.77–7.00 (dd, 2H, Ph)	356 (5) [M^+]; 233 (30); 206 (10); 191 (100); 177 (10); 123 (8); 91 (5); 79 (10); 57 (25); 41 (10)

* The total intensity of isotope peaks is given counted on 35 amu of chlorine. The ratio of particles with masses differing by two atomic units for chlorine-containing fragment peaks is 3 : 1, which corresponds to the natural content of ^{35}Cl and ^{37}Cl chlorine isotopes.

Found,%: C 57.12, H 5.22, Cl 30.70. Calculated for $C_{22}H_{24}Cl_4O_2$, %: C 57.16, H 5.23, Cl 30.68.

A mixture of p- and o-isomers (1.2 : 1): 4-[1-(2,2-(dichloro-1-methylcyclopropyl)ethyl]phenol (**IIIa**), 2-[1-(2,2-(dichloro-1-methylcyclopropyl)ethyl]phenol (**IIIb**):

Found,%: C 58.75, H 5.75, Cl 28.95. Calculated for $C_{24}H_{28}Cl_4O_2$, %: C 58.79, H 5.76, Cl 28.92.

2,6-di-*tert*-butyl-4-[1-(2,2-(dichlorocyclopropyl)ethyl]phenol (**IVa**):

Found,%: C 66.42, H 8.24, Cl 20.53. Calculated for $C_{19}H_{28}Cl_2O$, %: C 66.47, H 8.22, Cl 20.65.

2,6-di-*tert*-butyl-4-[1-(2,2-(dichloro-1-methylcyclopropyl)ethyl]phenol (**IVb**):

Found,%: C 67.18, H 8.41, Cl 19.79. Calculated for $C_{20}H_{30}Cl_2O$, %: C 67.22, H 8.46, Cl 19.84.

In summary, vinyl-*gem*-dichlorocyclopropanes can be successfully used as alkylating agents for the preparation of polyfunctional phenols containing the *gem*-dichlorocyclopropyl moiety.

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