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Synthesis of 1-(4-Isopropenylphenoxy)-bromo-C_2–C_4-alkanes and Application of Their Transformation Products

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Abstract—Reaction of 4-isopropenylphenol with α,ω-dibromo-C_2-C_4-alkanes by the Willamson reaction in the presence of potassium iodide as promoter, aiming to synthesize the corresponding monobromosubstituted derivatives and to study their some chemical transformation. Optimal conditions to obtain 1-(4-isopropenylphenoxy)-2-bromoethane, 1-(4-isopropenylphenoxy)-3-bromopropane and 1-(4-isopropenylphenoxy)-4-bromobutane were found. The nitrogen-containing derivatives, inhibitors of a hydrosulfuric corrosion in the water-salt solutions, were obtained on the basis of the first two compounds. The derivatives involving multiple bond and ester-group were synthesized from the third compound. Their incorporation into the polystyrene chains in the process synthesis gives them plasticize properties.

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Alkenylphenols and their derivatives are of quiet various uses [1–6]. Their reactions with halogen-containing alkanes by Willamson, in particular with symmetric dihalogenalkanes, promise interesting resultes. They enable synthesis of new phenol derivatives containing multiple bond C=C and halogen atom, and as a result they can be used as intermediate for the further transformations.

It was shown in the work [7] that di(4-isopropenylphenoxy)alkanes are dominantly formed by the reaction of 4-isopropenylphenol (4-IP) with α,ω-dihalogen-C_1–C_4-alkanes in the presence of potassium hydroxide. However, the further investigations showed that, among them, (4-isopropenylphenoxy)halogens were formed too. A study of an influence of such various factors as a temperature and ratio of reagents on the reaction progress has shown that the molar ratio of the used substances effects essentially on a composition of end products.

In this work we present results of studying the reactions of 1,2-dibromoethane (DBE), 1,3-dibromopropane (DBP) and 1,4-dibromobutane (DBB) with 4-IP for the purpose of synthesis of the corresponding bromoalkyl derivatives, and of studying their some transformations.

The reactions of DBE, DBP and DBB with 4-IP were carried out by Scheme 1.

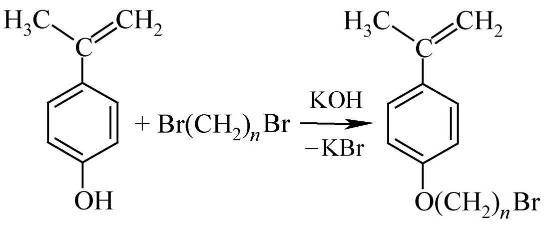
Results of performed investigation show, that the temperature and molar ratio of reagents in the mixture effect significantly on formation of the monobromosubstituted derivatives DBE, DBP and DBB.

Experiments for search of optimal conditions providing a good yield were conducted by the example of DBB and 4-IP at the different temperatures and molar ratio of DBB and 4-IP 1:1. We have found that as temperature is increased from 20 to 80°C the yield of monobromine-containing compound grows from 3.4 to 47.8%. Further temperature increase to 100°C leads to decrease in its yield to 45.1%. The side reaction of 4-IP dimerization enhances under these conditions.

An obtained dependence of 1-(4-isopropenylphenoxy)-4-bromobutane yield on the molar ratio DBB : 4-IP at the found optimal temperature 80°C are given on the figure.

The maximum yield, 64.2%, compound **III** was obtained at the molar ratio of DBB and 4-IP 1.5 : 1. Further increase of DBB amount in the initial mixture

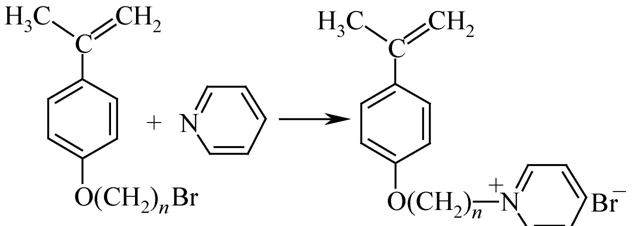
Scheme 1.



I–III

$n = 2$ (**I**), $n = 3$ (**II**), $n = 4$ (**III**).

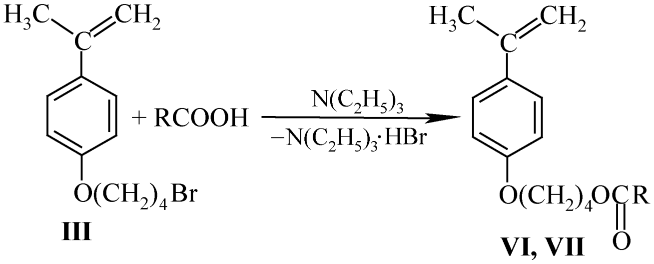
Scheme 2.



I, II **IV, V**

n = 2: 1-(4-isopropenylphenoxy)ethyl-*N*-pyridinium bromide **IV**, n = 3: 1-(4-isopropenylphenoxy)propyl-*N*-pyridinium bromide **V**.

Scheme 3.



RCOOH – $C_8H_{17}COOH$; naphthene acids frac-tion.

leads to no essential change in the yield of the end product.

Note that in the course of this reaction under the optimal conditions product **III** forms along with formation of approximately 18% of a disubstitution product, 1,4-di(4-isopropenylphenoxy)butane, and also little amounts of dimer derivatives of 4-IP (~4%).

The presence of the halogen atom in the structure of compounds **I–III** enables their further transformation with pyridine and organic acids.

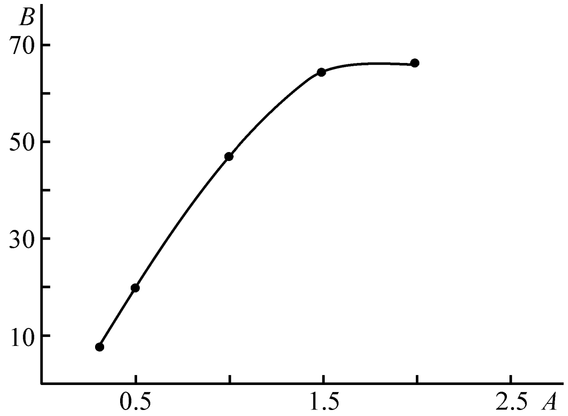
Quaternization of **I** and **II** with pyridine at 110°C for 5 h results in the corresponding quaternary salts **IV** and **V** (Scheme 2).

Synthesis of compound **III** derivatives containing ester-group was carried out by reaction of **III** with pelargonic acid and commercial fraction of naphthene acids. The reaction proceeds in acetone in the presence of triethylamine as acceptor of HBr at room temperature (Scheme 3).

Studying of the esterification reaction of compound **III** with pelargonic acid makes it possible to establish, as one would expected, that this process occurs with participation of the bromine-containing fragment to form compounds containing ester-group and multiple bond simultaneously.

The investigation of compounds **IV** and **V** as corrosion inhibitors for steel St.3 showed that they possessed high inhibiting properties in the examined aggressive media (see the table).

It is known [8] that the presence of multiple bond and quaternary pyridinium fragments in the inhibitor structure contributes to their surface activity on a metal to form the sufficiently fast adsorption layers protecting its against corrosion. Addition of the aforementioned compounds to the aqueous-saline solution, saturated with hydrogen sulfide, even in minimum concentration (25–50 mg l^{-1}) provides a protecting effect: 63.0 and 73.3% for **IV,** and 76.5 and 82.3% for **V**. A concentration increase to 150–200 mg l^{-1} make it possible to decrease essentially the corrosion rate and to increase the protecting degree on average to 95–99%. Compound **V** exceeds **IV** in an efficiency of the protection.



Effect of the ratio DBB and 4-IP (*A*) on the yield of 1-(4-iso-propenylphenoxy)-4-bromobutane *B* (%) (temperature 80°C).

Results of tests of 1-(4-isopropenylphenoxy)ethyl- (**IV**) and 1-(4-isopropenylphenoxy)propyl-N-pyridinium bromides (**V**) as SRB bactericides and hydrosulfuric corrosion inhibitors for steel St.3

Reagent	*c*, mg l^{-1}	Suppression degree of SRB growth, %	Corrosion rate,[a] g m^{-2} h^{-1}	Protection degree,[a] %
IV	10	23.0	1.430	47.5
	25	35.0	0.899	63.0
	50	48.0	0.649	73.3
	75	50.0	0.486	80.0
	100	73.0	0.328	86.5
	125	90.0	0.211	91.3
	150	100	0.121	95.0
	175	100	0.049	98.0
	200	100	0.024	99.0
V	10	51.0	0.720	70.3
	25	67.0	0.570	76.5
	50	80.0	0.430	82.3
	75	93.5	0.301	87.6
	100	100	0.085	96.5
	150	100	0.049	98.0
	200	100	0.013	99.5
without reagents	–	–	2.430	-

[a] 3% NaCl + white spirit + 500 mg l^{-1} H_2S, pH 5.3, *t* 25°C.

Research of compounds **IV** and **V** in the different concentrations as bactericides suppressing growth of sulfate-reducing bacteria (SRB) showed that the bacteria growth is virtually suppressed when compound **IV** is used in the concentration of 150 mg l^{-1}, **V**, in the concentration of 100 mg l^{-1}. Their applying in the lower concentrations allows canceling no fully a bacteria growth: compound **IV** (50–75 mg l^{-1}) decreases SRB growth on average by 50% and product **V** in the same concentration, by 80–93.5%.

For search of possible ways for practical use of compounds **VII** as comonomer-plasticizer containing isopropenyl and ester-groups simultaneously, we studied reaction of their copolymerization with styrene in the ratios from 5 : 95 to 30 : 70 (wt %). The process was carried out in a camera in the presence of 0.5% of di-*tert*-butylperoxide as initiator at 120°C for 20 h. It was found that the ratio of the taken monomers in the initial mixture effected essentially on the yield of the end copolymer. The copolymer yield was 97.6, 94.2, 88.3 and 71.0% at the ratio 5 : 95, 10 : 90, 20 : 80 and 30 : 70 (wt %), respectively. The obtained results testify that styrene is more reactive than the derivatives of compound **III** involving ester-group. If their fraction in the starting mixture is increased from 5 to 30%, the copolymerization rate decreases. Total quantity of the unreacted monomers is about 29%.

Values of a characteristic viscosity of 0.4% solutions of copolymers in toluene are decreased from 0.45 to 0.33 by the same sequence, i.e. in the case of the growth of the quantity of monomers **VII** in the initial mixture the chain-breaking reactions intensify.

According to results of preliminary tests of the obtained copolymers, an introduction of small amounts of monomer **VII** into the polystyrene chains gives to them the plasticizing properties (an elasticity of film on the metal 3–5 mm, against 10 mm for the polystyrene).

Hence, the conducted researches allow conclusion that the compounds **I–III** containing bromine atom and isopropenyl group may be used as semi-products for realization of various chemical transformations for preparation new chemically important products with useful properties.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer (operating frequency 300 and 75 MHz respectively, internal standard TMS. IR spectra were registered on a Varian 3600 FT-IR spectrometer.

Compounds I–III. Potassium 4-isopropenylphenolate obtained by the reaction of 0.1 mol of 4-IP with 0.1 mol of KOH alcohol solution, at 80°C was added dropwise to 0.15 mol of dibromo-C_2–C_4-alkane containing several grains of KI as promoter. The weight ratio KOH : isopropanol was 1 : 20. This mixture was stirred at the same temperature for 0.5 h. In the course of reaction the white crystalline precipitate of di(4-isopropenylphenoxy)-C_2–C_4-alkane was formed along with a side inorganic salt. The target compound 1-(4-isopropenylphenoxy)bromo-C_2–C_4-alkane **I–III** remained in the isopropanol solution. It was extracted from alcohol by treatment with distilled water. In this case viscous pale yellow mass formed. It was dissolved into benzene and washed with water to neutral reaction. Benzene and unreacted dibromo-C_2–C_4-alkane were evaporated. Compounds **I–III** were extracted with hexane to remove admixtures. Yields of compounds **I–III** were 31.6, 51.8, and 64.2%, respectively. They are white substances, very soluble in acetone, benzene, CCl_4 and alcohols, mp 32, 35 and 37°C, respectively.

Quaternization reaction of I and II with pyridine were carried out in toluene medium. Compound **I** or **II** (0.06 mol) was dissolved in 40 ml of toluene; this solution was added dropwise into a flask charged with 7.1 g (0.09 mol) of the freshly distilled pyridine. The mixture was refluxed for 5 h at 110°C. The reaction product was precipitated. It was filtered off, washed carefully with acetone and evacuated. Yields 70.2 (**IV**) and 74.0% (**V**), pale yellow substances, very soluble in water.

The compound III derivatives containing ester-group were obtained by reaction of **III** with pelargonic acid and commercial fraction of naphthene acids in acetone in the presence of triethylamine as HBr acceptor at room temperature. To 10.1 g (0.1 mol) of triethylamine dissolved in 20 ml of acetone was added pelargonic acid to a weak-acidic medium. This stirred mixture was added to a solution of 13.45 g (0.05 mol) of compound **III** in 60 ml of acetone and was maintained at room temperature for 5 h. This solution was filtered off from triethylammonium bromide and diluted with 100 ml of the distilled water to form a precipitate. The latter was dissolved into benzene and washed carefully with aqueous solution of 5% sodium bicarbonate to neutral medium. Benzene solution was dried over anhydrous sodium sulfate, concentrated and distilled to form 1-(4-isopropenylphenoxy)butylpelargonate **VI** as a transparent viscous pale yellow substance. Yield 73.4%.

The product **III** derivative **VII** with ester group was obtained under the found conditions using **III** and commercial fraction of naphthene acids (bp 150–170°C/15 mm Hg) in yield of 68%; d_{20} 971.8 kg m^{-3}, n_D^{20} 1.4935.

1-(4-Isopropenylphenoxy)-2-bromoethane (I). ^{1}H NMR spectrum (DMSO-d_6, δ, ppm): 2.08 s (3H, CH_3), 3.78 t (2H, CH_2Br), 4.32 t (2H, CH_2O), 4.99 and 5.35 s (2H, =CH_2), 6.93 and 7.45 d (4H, Ar). ^{13}C NMR spectrum (DMSO-d_6, δ, ppm): 23.4, 33.2, 68.4, 112.8, 114.7, 127.4, 138.6, 143.5, 157.8.

1-(4- Isopropenylphenoxy)-3-bromopropane (II). ^{1}H NMR spectrum (CCl_4, δ, ppm): 2.1 s (3H, CH_3), 2.3 m (2H, CH_2), 3.38 t (2H, CH_2Br), 4.19 t (2H, CH_2O), 4.97 and 5.2 s (2H, =CH_2), 6.85 d (2H, Ar), 7.35 d (2H, Ar). ^{13}C NMR spectrum (CCl_4, δ, ppm): 22.8, 27.5, 34.3, 67.9, 112.5, 115.2, 128.5, 135.4, 144.3, 156.7. IR spectrum, ν, (cm^{-1}): 2960, 2871, 1471, 1384, 743 (CH_3; CH_2); 827 (1,4–Ar); 1255, 1030 (Ph–O–C); 1645, 887 (C=CH_2);

549 (C–Br).

1-(4- Isopropenylphenoxy)-4-bromobutane (III). ^{1}H NMR spectrum (CCl_4, δ, ppm): 1.88–2.1 m (4H, $2CH_2$), 2.12 s (3H, CH_3), 3.42 t (2H, CH_2Br), 3.95 t (2H, CH_2O), 4.92 and 5.22 s (2H, $=CH_2$), 6.75 d (2H, Ar), 7.31 d (2H, Ar). ^{13}C NMR spectrum (CCl_4, δ, ppm): 21.9, 27.5, 28.8, 32.4, 66.6, 110.5, 113.4, 126.5, 134.6, 142.2, 145.1, 156.9. IR spectrum, ν, (cm^{-1}): 2944, 2873, 1473, 1385, 744 (CH_3; CH_2); 1646, 886 ($C=CH_2$); 3041, 1575, 1473, 837 (Ar); 1247, 1043 (C–O–C); 548 (C–Br).

1-(4- Isopropenylphenoxy)ethyl-*N*-pyridinium bromide (IV). ^{1}H NMR spectrum (D_2O, δ, ppm): 1.79 s (3H, CH_3), 2.47 m (2H, CH_2) 4.36 t (2H, OCH_2), 4.75 and 5.05 s (2H, $=CH_2$), 4.9 t (2H, NCH_2), 6.94 and 7.38 d (4H, arom.), 8.27, 8.75 and 9.55 (5 H, Py). ^{13}C NMR spectrum (CCl_4, δ, ppm): 21.7, 29.7, 61.2, 67.6, 110.1, 114.9, 126.9, 127.4, 124.8, 142.8, 144.3, 146.4, 157.2.

1-(4- Isopropenylphenoxy)propyl-*N*-pyridinium bromide (V). ^{1}H NMR spectrum (D_2O, δ, ppm): 1.79 s (3H, CH_3), 4.35 t (2H, OCH_2), 4.75 and 5.05 s (2H, $=CH_2$), 4.78 t (2H, NCH_2), 6.7 d (2H, Ar), 7.15 d (2H, Ar), 7.79 t (2H, Py), 8.35 t (1 H, Py), 8.8 d (2H, Py). ^{13}C NMR spectrum (CCl_4, δ, ppm): 21.7, 61.8, 66.7, 111.9, 114.5, 127.3, 128.4, 134.4, 142.6, 146.2, 156.8.

1-(4- Isopropenylphenoxy)butylpellargonate (VI). ^{1}H NMR spectrum (CCl_4, δ, ppm): 0.89 t (3H, CH_3), 1.25 m (10H, $5CH_2$), 1.59 m (2H, CH_2), 2.09 m (4H, $2CH_2$), 2.1 s (3H, CH_3), 2.25 t (2H, CH_2–C=O), 3.93 t (2H, CH_2O), 4.12 t (2H, CH_2O), 4.92 and 5.23 s (2H, $=CH_2$), 6.78 d (2H, Ar), 7.32 d (2H, Ar). ^{13}C NMR spectrum (CCl_4, δ, ppm): 14.1, 21.9, 22.6, 25.2, 25.7, 27.4, 28.8, 29.3, 30.9, 34.6, 61.2, 66.7, 111.3, 114.8, 126.7, 134.8, 142.7, 156.8, 164.8.

In the IR spectrum of compound **VII** following characteristic bands were found (cm^{-1}): 3050, 2944, 2880, 1456, 1376, 744 (CH_3; CH_2); 1648, 884 ($C=CH_2$); 3045, 1584, 1492, 832 (Ar); 1248, 1084, 1043 (C–O–C); 1740 (C=O). They confirm that esterification product was formed.

Copolymers structures were also determined using IR spectra containing characteristic absorption bands (cm^{-1}): 2972, 2850, 1452, 1375, 756 (CH_3; CH_2); 3060, 1583, 1492, 827, 756, 695 (Ar); 1245, 1068, 1028 (C–O–C); 1734 (C=O).

Compounds **IV** and **V** were tested as corrosion inhibitors for steel St.3 in aggressive media containing H_2S, SRB, salts and others substances. The bactericide activity was estimated by determining of suppression degree of SRB growth by the known procedure [9]. Accumulating cultures isolated from oil stratal water (sea petroleum deposit Gyuneshli) were used in the study.

Some quantity of the tested reagent was added into produced water and was kept for 24 h at 32°C. Further the samples by 1–2 ml were taken and charged into bottles with the Postgate nutrient medium, which also were kept for a long time (15 days) at 32°C. Hydrogen sulfide content was determined at the end of the experiment. Experiments with samples without reagents, inhibitors, were conducted under the same conditions to compare. An efficiency of sulfate-reduction was evaluated by the samples darkening and the suppression degree of SRB growth.

Inhibiting properties of compounds **IV** and **V** were examined in the system containing 3% NaCl aqueous solution and white spirit (the ratio 7 : 1 vol.) saturated with hydrogen sulfide (500 mg l^{-1}). These researches were performed by gravimetric method in a dynamic mode at 25°C.

CONCLUSIONS

(1) 1-(4-Isopropenylphenoxy)-2-bromethane, 1-(4-isopropenylphenoxy)-3-bromopropane and 1-(4-isopropenylphenoxy)-4-bromobutane were obtained by reaction of 4-isopropenylphenol with α,ω-dibromo-C_2–C_4-alkanes in yield of 31.5, 51.8 and 64.2% respectively.

(2) On the basis of the reaction with pyridine and organic acids was prepared number of the new compounds containing in the structure multiple C=C bond and nitrogen atom or multiple bond C=C and ester group simultaneously.

(3) Compounds with multiple bond C=C and nitrogen atom possess high protective properties and can be used as inhibitors of hydrosulfuric corrosion of steel. Compounds containing multiple bond C=C and ester group may be used as plasticizing monomers for styrene polymers.

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