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Abstract

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ALKYLATION OF 4-FLUOROPHENOL WITH PROPYLENE AND CYCLOHEXENE IN THE PRESENCE OF THE CATALYSTS $BF_3 \cdot H_3PO_4$ AND $BF_3 \cdot O(C_2H_5)_2$

The reaction of fluorophenols with olefins has not been covered at all in the literature. In continuation of investigations in the field of the alkylation of halophenols with olefins in the presence of catalysts based on boron fluoride ([1-6]), the present communication studies the reaction of 4-fluorophenol with propylene and cyclohexene in the presence of $BF_3 \cdot H_3PO_4$ and $BF_3 \cdot O(C_2H_5)_2$.

4-Fluorophenol, in contrast to the chloro- and bromophenols studied earlier, possesses higher reactivity and, on interaction with olefins, in particular with propylene, forms a rather complex mixture of products. In the present case, along with the isopropyl ether of 4-fluorophenol, the isopropyl ether of isopropylfluorophenol is constantly formed, and under certain conditions isopropylfluorophenol is also obtained. The yields of the products depend on the nature and amount of catalyst, the temperature, and the molar ratios of the reactants. Thus, in the presence of $BF_3 \cdot O(C_2H_5)_2$, as the mildest catalyst, at a temperature of 60° only ether products are obtained, and phenolic products are absent, at least in appreciable quantities. In the presence of $BF_3 \cdot H_3PO_4$ the yields of phenolic compounds are the higher, the higher the temperature within the range from 40 to 70°.

The best conditions under which the isopropyl ether of 4-fluorophenol is obtained in 54% yield are molar ratios of fluorophenol, propylene, and $BF_3 \cdot H_3PO_4$ equal to 3 : 1 : 0.4 and a temperature of 40°; for obtaining the isopropyl ether of isopropyl-4-fluorophenol in 36% yield, the ratios of reactants and catalyst are 5 : 1 : 0.3 and the temperature is 60°; and for obtaining isopropyl-4-fluorophenol in a maximum yield of 38%, the ratios of reactants and catalyst are 3 : 1 : 0.2 and the temperature is 70°.

The influence of temperature, catalyst quantities, and molar ratios of the reactants on the total yield of the indicated products is seen from the data of the experiments given in Table 1.

4-Fluorophenol with cyclohexene in the presence of $BF_3 \cdot H_3PO_4$ forms a single product—the cyclohexyl ether of 4-fluorophenol—with a maximum yield of 70.7%

of theoretical. After the very first distillation of the alkylate, the product boils within a range of 2–3°, as is seen from the data in Table 2. Compounds of the ether type were identified by cleavage to the corresponding phenols and conversion of the latter into phenoxyacetic acids.

Experimental Part

4-Fluorophenol was obtained by demethylation of 4-fluoroanisole ([7]), m.p. 46. Propylene, cyclohexene, and the catalysts were obtained as before ([5]).

Alkylation of 4-fluorophenol with propylene. The reaction was carried out by the usual procedure ([6]) in a three-necked flask. In experiments with the ethyl etherate of boron fluoride, fluorophenol and catalyst were placed in the flask, the mixture was heated to 60°, and, with vigorous stirring, propylene was introduced at a rate of 1.2–2 l/hr. As the propylene was introduced, the reaction mass became brown in color and by the end acquired a dark-brown coloration. After the calculated amount of propylene had been passed through,

Table 1

Alkylation of 4-fluorophenol with propylene in the presence of $BF_3 \cdot H_3PO_4$ and $BF_3 \cdot O(C_2H_5)_2$

Experiment no.	Molar ratios of fluorophenol, propylene, and catalyst	Reaction temperature, °C	Duration of propylene introduction, h	4-Fluorophenol isopropyl ether, % of theory	4-Fluorophenol isopropyl ether, boiling range, °C/mm	4-Fluorophenol isopropyl ether, n_D^{20}	2-Isopropyl-4-fluorophenol, % of theory	2-Isopropyl-4-fluorophenol, boiling range, °C/mm	2-Isopropyl-4-fluorophenol, n_D^{20}	2-Isopropyl-4-fluorophenol, % of theory	2-Isopropyl-4-fluorophenol, boiling range, °C/mm	2-Isopropyl-4-fluorophenol, n_D^{20}
1	2 : 1 : 0.2	60	2	8.3	37—50/3	1.4755	28.5	71—80/4	1.4912			
2	2 : 1 : 0.4	60	2.5	0.5	42—44/2	1.4753	25.8	88—96/8	1.4923			

Experiment no.	Molar ratios of fluorophenol, propylene, and catalyst: $BF_3 \cdot H_3PO_4$	Reaction temperature, °C	Duration of propylene introduction, h	4-Fluorophenol isopropyl ether, % of theory	4-Fluorophenol isopropyl ether, boiling range, °C/mm	4-Fluorophenol isopropyl ether, n_D^{20}	2-Isopropyl-4-fluorophenol, % of theory	2-Isopropyl-4-fluorophenol, boiling range, °C/mm	2-Isopropyl-4-fluorophenol, n_D^{20}	2-Isopropyl-4-fluorophenol, % of theory	2-Isopropyl-4-fluorophenol, boiling range, °C/mm	2-Isopropyl-4-fluorophenol, n_D^{20}
3	2 : 1 : 0.4	40	2	28.3	56–60/6	1.4748	29.6	82–90/7	1.4910	16.4	80–85/5	1.5040
4	3 : 1 : 0.1	40	7	42.4	52–60/5	1.4750	16.4	77–82/6	1.4930	12.0	80–85/5	1.5042
5	3 : 1 : 0.2	40	2.5	41.1	53–60/6	1.4760	28.8	76–82/6	1.4937			
6	3 : 1 : 0.2	50	2	38.8	44–47/4	1.4750	25.8	73–80/4	1.4922			
7	3 : 1 : 0.2	60	4	52.3	46–52/4	1.4758	33.2	74–80/4	1.4912	5.8	81–86/5	1.5022
8	3 : 1 : 0.2	70	2	4.6	56–60/6	1.4748	32.9	82–90/7	1.4928	38.1	78–81/4	1.5045
9	3 : 1 : 0.3	40	2	50.6	40–46/2	1.4750	29.9	71–80/3	1.4913			
10	3 : 1 : 0.4	40	1.5	54.0	44–50/3	1.4754	23.1	72–80/3	1.4920			
11	4 : 1 : 0.4	40	3	45.5	56–60/6	1.4750	31.0	82–90/7	1.4910	5.3	80–87/6	1.5028
12	5 : 1 : 0.3	60	2	30.8	52–60/5	1.4753	36.3	79–85/6	1.4920	10.4	82–88/6	1.5020

Experiment no.	Molar ratios of fluorophenol, propylene, and catalyst	Reaction temperature, °C	Duration of propylene introduction, h	4-Fluorophenol isopropyl ether, % of theory	4-Fluorophenol isopropyl ether, boiling range, °C/mm	n_D^{20}	2-Isopropyl-4-fluorophenol, % of theory	2-Isopropyl-4-fluorophenol, boiling range, °C/mm	n_D^{20}	2-Isopropyl-4-fluorophenol, % of theory	2-Isopropyl-4-fluorophenol, boiling range, °C/mm	n_D^{20}
13	$BF_3 \cdot H_3PO_4$ 5 : 1 : 0.4	60	2	19.1	52—60/5	1.4756	28.0	80—84/6	1.4917	32.4	81—87/6	1.5040

Note. For each experiment, 0.1–0.2 mole of propylene and the calculated amounts of 4-fluorophenol and catalyst were taken. Experiments nos. 1 and 2 were carried out in the presence of boron fluoride ethyl etherate. The temperature fluctuated by ±2° from that indicated in the table.

the mixture was stirred for 2 hr at the experimental temperature and left to stand at room temperature for 12 hr. Then, in the form of a rather viscous oil, it was mixed with benzene and treated repeatedly with small portions of 10% aqueous NaOH solution until complete extraction of the phenolic products (test with a drop of hydrochloric acid). The ether products, in the form of a transparent, almost colorless oil, were washed well with water, dried over calcium chloride, and distilled into fractions boiling within the range of 2 to 10°. The phenolic products, soluble in alkali, were treated with conc. HCl, extracted with ether, dried over sodium sulfate, and likewise distilled within a range of 3–6°. For identification, both were redistilled into narrower fractions. By heating with HBr, the isopropyl ether of 2-isopropyl-4-fluorophenol was converted into 2-isopropyl-4-fluorophenol, and from the latter, with chloroacetic acid, 2-isopropyl-4-fluorophenoxyacetic acid was obtained.

Table 2

Alkylation of 4-fluorophenol with cyclohexene in the presence of $BF_3 \cdot H_3PO_4$

No. of experiments	Molar ratio: 4-fluorophenol, cyclohexene, and $BF_3 \cdot H_3PO_4$	Reaction temperature, °C	Reaction time, min	Cyclohexyl ether of 4-fluorophenol, % of theoretical	Cyclohexyl ether of 4-fluorophenol, boiling range, °C/mm	Cyclohexyl ether of 4-fluorophenol, n_D^{20}
1	2 : 1 : 0.2	40	40	63.5	88-90/2	1.5065
2	3 : 1 : 0.1	40	40	63.7	90-94/3	1.5065
3	3 : 1 : 0.2	40	50	70.7	84-86/1	1.5068
4	3 : 1 : 0.2	60	60	64.2	88-92/2	1.5066
5	3 : 1 : 0.3	40	60	59.3	82-85/1	1.5066

Alkylation of 4-fluorophenol with cyclohexene. The reaction was carried out in a three-necked flask with vigorous stirring. To a mixture of 4-fluorophenol and the catalyst $BF_3 \cdot H_3PO_4$, heated to a specified temperature, 0.1 mole of cyclohexene was slowly added from a dropping funnel. The reaction mass, a brown liquid, was treated in the same way as in the reaction with propylene. In this case the sole reaction product is the cyclohexyl ether of 4-fluorophenol, which already during the first distillation of the alkylate is isolated in fairly pure form. After redistillation it is a colorless oil with a pleasant ether-like odor. The physicochemical constants of the products obtained are given in Table 3.

Table 3

Compounds	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.
Isopropyl ether of 4-fluorophenol	49/4	1.0340	1.4745	41.90	41.59
Isopropyl ether of 2-isopropyl-4-fluorophenol	77.5-78/5	1.0284	1.4906	55.18	55.44
2-Isopropyl-4-fluorophenol	81-82/6	1.0942	1.5047	41.69	41.48

Compounds	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.
2-Isopropyl-4-fluorophenoxyacetic acid	m.p. 124°				
Cyclohexyl ether of 4-fluorophenol	95–96/3	1.0767	1.5070	53.70	53.36

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Note: Figure translations are in progress. See original paper for figures.