Academy of Sciences of the USSR Reports

Academician A. V. TOPCHIEV, B. M. TUMERMAN, and T. A. FEDOROVA

1958

SovietRxiv

Abstract

Full Text

Academy of Sciences of the USSR Reports
1958. Volume 120, No. 1

CHEMISTRY

Academician A. V. TOPCHIEV, B. M. TUMERMAN, and T. A. FEDOROVA

ALKYLATION OF PHENOL WITH DIISOBUTYLENE AND TRIISOBUTYLENE IN THE PRESENCE OF CATALYSTS CONTAINING BORON FLUORIDE

As has already been reported ([1]), the alkylation of phenols with lower olefins, isobutylene, and isoamylene in the presence of catalysts containing boron fluoride proceeds in high yield. This made it possible for us to assume that such catalysts as the ethyl etherate of boron fluoride $(C_2H_5)_2O \cdot BF_3$, orthophosphoric acid saturated with boron fluoride $H_3PO_4 \cdot BF_3$, and the monohydrate of boron fluoride $H_2O \cdot BF_3$ would also prove to be active catalysts in the alkylation of phenol with diisobutylene C_8H_{16} and triisobutylene $C_{12}H_{24}$.

The alkylating hydrocarbons diisobutylene and triisobutylene were obtained by polymerization of isobutylene in the presence of the ethyl etherate of boron fluoride. The method for obtaining diisobutylene and triisobutylene and their structure have been published ([2 3]). Principal constants: for diisobutylene, b.p. 100–110°, n_D^{20} 1.4105, d_{20}^{20} 0.7216, aniline point 40; for triisobutylene, b.p. 175–180°, aniline point 73.5, n_D^{20} 1.4329, d_{20}^{20} 0.7216.

The catalysts—the ethyl etherate of boron fluoride, orthophosphoric acid saturated with boron fluoride, and the monohydrate of boron fluoride—were obtained by passing gaseous boron fluoride through diethyl ether, orthophosphoric acid, and water. In the interaction of gaseous boron fluoride with diethyl ether, orthophosphoric acid, and water, molecular compounds of these substances are formed. Their preparation, physicochemical characterization, and catalytic action have been described ([4]).

In a series of experiments the yield of alkylate (*n*-tert-octylphenol and dodecylphenol) was studied as a function of the nature of the catalyst, its optimum amount, the reaction temperature, the duration of the reaction, and the ratio of the reacting components.

The experiments were carried out as follows. Into a round-bottomed three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel, freshly distilled molten phenol was charged in an amount of 50 g (0.5 mole). To the phenol were added various amounts of the catalysts under study (see Table 1). After this the stirrer was switched on and 30 g of diisobutylene (0.5 mole per mole of phenol) or triisobutylene was added dropwise, the ratio being varied from 0.5 to 1 mole per mole of phenol. With continuous stirring of the mixture, the temperature was maintained constant.

After completion of the reaction, the reaction mixture was washed in a separatory funnel with hot water until neutral to Congo red, dried over calcium chloride, and subjected to distillation in vacuum (10 mm residual pressure).

Alkylation of phenol with diisobutylene and triisobutylene in the presence of ethyl etherate

Table 1

Effect of the amount of catalyst $(C_2H_5)_2O \cdot BF_3$, temperature, and duration of the experiment on the alkylation of phenol with diisobutylene

Phenol, g	Diisobutylene, g	Catalyst, g	Catalyst, %	Temp., °C	Time, h	Phenol	Alkylate	Residue	Loss
50	30	2.5	10	50	2	16.2	76.0	5.9	1.9
50	30	1.25	5	50	2	15	76.5	6.0	2.5
50	30	0.25	1	50	2	19	73.6	4.9	2.5
50	30	0.25	1	70	2	37	54.6	5.1	3.9
50	50	0.25	1	70	3	53	40.6	30	4.0

boron fluoride $(C_2H_5)_2O \cdot BF_3$. The reaction was carried out by the procedure described above. In this series of experiments, in the alkylation of phenol with diisobutylene, the amount of catalyst, the temperature of the experiments, and the duration of the experiments were varied (Table 1).

In the alkylation of phenol with triisobutylene, the yield of alkylate was studied as a function of the amount of catalyst, the temperature, the duration of the experiment, and the ratio of olefin to phenol (see Figs. 1–3).

It is evident from Table 1 that the yield of alkylate increases as the amount of catalyst is increased from 1 to 5% based on phenol. Increasing the amount of catalyst to 10% does not increase the yield of alkylate. Raising the reaction temperature, as well as increasing the reaction time, decreases the yield of alkylate.

As can be seen from Fig. 2, the yield of alkylate increases as the amount of catalyst is increased from 1 to 5%. The optimal conditions for carrying out the alkylation reaction of phenol with triisobutylene are as follows: experiment time 3 h, temperature 70°, catalyst amount 5% based on phenol.

Fig. 1. Yield of alkylate as a function of temperature. Catalysts: a –$H_3PO_4 \cdot BF_3$ (10%), b –$H_2O \cdot BF_3$ (10%)

Figure 1: Fig. 1. Yield of alkylate as a function of temperature. Catalysts: a –$H_3PO_4 \cdot BF_3$ (10%), b –$H_2O \cdot BF_3$ (10%)

Fig. 2

Figure 2: Fig. 2

Alkylation of phenol with diisobutylene and triisobutylene in the presence of orthophosphoric acid saturated with boron fluoride $H_3PO_4 \cdot BF_3$**, and boron fluoride monohydrate** $H_2O \cdot BF_3$**.** The procedure for carrying out the experiments was not changed.

Fig. 1. Yield of alkylate as a function of temperature. Catalysts: *a* –$H_3PO_4 \cdot BF_3$ (10%), *b* –$H_2O \cdot BF_3$ (10%).

Table 2

Effect of the amount of catalyst $H_3PO_4 \cdot BF_3$, temperature, and duration of the experiment on the alkylation of phenol with diisobutylene

Phenol, g	Diisobutylene, g	Catalyst, %	Temp., °C	Time, h	Phenol	Alkylate	Residue	Loss
50	30	5	100	4	38.2	54.5	5.0	2.3
50	30	1	100	4	38	54.9	4.8	2.1
50	30	1	50	2	45.0	48.0	4.0	3.0
50	30	2	50	2	45.1	47.9	4.1	2.9

The results of this series of experiments on the alkylation of phenol with diisobutylene are given in Table 2, and with triisobutylene–in Figs. 1 and 3.

It is seen from Table 2 that, when the reaction temperature is raised from 50 to 100°, the amount of catalyst from 1 to 5%, and the duration of the experiment from 2 to 4 hours, the yield of alkylate increases by 5%.

The alkylation of phenol with diisobutylene in the presence of boron fluoride monohydrate was carried out under the optimum conditions for $H_3PO_4 \cdot BF_3$.

Fig. 2. Yield of alkylate as a function of the amount of catalyst $(C_2H_5)_2OBF_3$ (70°, 3 hours.)

Fig. 3. Yield of alkylate as a function of the duration of the experiment. Catalysts: **a**–$(C_2H_5)_2 \cdot BF_3$ (10%, 70°), **b**–$H_2O \cdot BF_3$ (20%, 50°), **c**–$H_3PO_4 \cdot BF_3$ (10%, 100°)

50 g of phenol and 30 g of diisobutylene were taken; the experimental temperature was 50°, the duration of the experiment 2 hours; the yield of alkylate was

Fig. 3

Figure 3: Fig. 3

then 38% of theory. The results of the alkylation of phenol with triisobutylene are given in Figs. 1 and 3, which show that the yield of alkylate (catalyst $H_3PO_4 \cdot BF_3$) increases with an increase in the amount of catalyst from 5 to 10%, and with an increase in the duration of the experiment from 1 to 4 hours. When the catalyst $H_2O \cdot BF_3$ is used, the yield of alkylate increases when the temperature is raised from 25 to 50°, but at 100° it decreases considerably.

Investigation of the alkylation products. The obtained *p*-tert.-octylphenol was washed with hot water to neutral reaction on Congo paper, dried, and distilled in vacuum at 10 mm residual pressure. Oil-like and crystalline products were obtained.

The crystalline products were recrystallized repeatedly from ethyl alcohol or isooctane. Recrystallization from acetic acid and normal heptane did not give good results. After recrystallization from isooctane, octylphenol melted at 68–70° (melting point of pure octylphenol 73–74°).

The oil-like products, representing the corresponding ethers of phenols, were not studied in detail.

Properties of *p*-tert.-octylphenol: b.p. 100–154°; $M = 210$; m.p. 68–70°; OH (by Tseretvinov) 5%.

The obtained dodecylphenol, washed with hot water to neutral reaction on Congo paper, was distilled in vacuum (5 mm residual pressure). Fractions 100-150 (crystals) and 150-165 (oil-like) were obtained. The crystalline fraction was recrystallized from ethyl alcohol. Dodecylphenol melted at 62-64°.

Properties of the dodecylphenol fractions: fraction I, b.p. 100–155°/5 mm, $M = 258$, m.p. 62–64°, OH (by Terevitinov) 6.1%; fraction II 155–165°/5 mm, $M = 262$.

Received
19 X 1957

REFERENCES

1. A. V. Topchiev, B. M. Tumerman, V. N. Andronov, L. N. Korshunova, *Neft. khoz.*, No. 7 (1954).
2. A. V. Topchiev, B. M. Tumerman, V. N. Andronov, DAN, 74, No. 1 (1950).
3. A. V. Topchiev, B. M. Tumerman, V. N. Andronov, DAN, 74, No. 3 (1950).
4. A. V. Topchiev, Ya. M. Paushkin, O. V. Zavgorodnii, *Usp. khim.*, 21, issue 4 (1952).

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