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Abstract

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ALKYLATION OF DIPHENYL WITH PSEUDOBUTYLENE IN THE PRESENCE OF THE CATALYST $BF_3 \cdot H_3PO_4$

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In continuation of earlier investigations in the field of alkylation of aromatic compounds with olefins in the presence of boron fluoride-based catalysts, we have studied the interaction of diphenyl with pseudobutylene in the presence of $BF_3 \cdot H_3PO_4$. The reaction was studied at various molar ratios of diphenyl, pseudobutylene, and catalyst, without a solvent and in CCl_4 solvent, over the temperature range 50–100°. The investigations established that diphenyl is alkylated by pseudobutylene in the presence of $BF_3 \cdot H_3PO_4$ at molar ratios equal to 1–4 : 1 : 0.2–0.3 at 50–100°, with monobutyldiphenyls being formed as the principal products. At temperatures of 70° and higher the process is accompanied by isomerization of pseudobutylene to isobutylene and leads to the formation of a mixture of *n*-sec-butyldiphenyl and *n*-tert-butyldiphenyl. Their relative amounts depend on the temperature and other factors. For example, when diphenyl is allowed to react with pseudobutylene and $BF_3H_3PO_4$ in molar ratios equal to 1 : 1 : 0.2, at a temperature of 70° and a pseudobutylene introduction rate of 5.5–6 l/hr, monobutyldiphenyls are obtained in a yield of 46.4% of theory. The relative content in the mixture of secondary and tertiary butyldiphenyls is, respectively, 81 and 19%. With approximately the same yield (47.2%), sec-butyldiphenyl and tert-butyldiphenyl are obtained at a temperature of 90°, but their relative amounts in the mixture change and are, respectively, 58 and 42%. At a reagent and catalyst ratio of 2 : 1 : 0.2 and a temperature of 90°, monobutyldiphenyls are formed in an overall yield of 38.8% of theory and with a relative content in the mixture of *n*-sec-butyldiphenyl of 74% and *n*-tert-butyldiphenyl of 26%.

The most favorable conditions, under which monobutyldiphenyls are obtained in a yield of 58–60% of theory and with a relative content in the alkylate of up to 92%, are molar ratios of diphenyl, pseudobutylene, and $BF_3 \cdot H_3PO_4$ equal to 1.75 : 1 : 0.25, a temperature of 90°, and a pseudobutylene introduction rate of 2.5–3 l/hr.

Reducing the catalyst to 0.13 mole under the indicated conditions lowers the yield of monobutyldiphenyls to 32%. Increasing the amount of diphenyl to 3 and 4 moles per mole of pseudobutylene also lowers the yield of monobutyldiphenyls

to 19–29%, but under these conditions polybutyldiphenyls are practically absent from the alkylate. When the reagents and catalyst are used in the ratio 1 : 1 : 0.2, monobutyldiphenyls are obtained in a yield of 43–45% and polybutyldiphenyls of 7–8% of theory.

Alkylation of diphenyl with pseudobutylene in CCl_4 solvent proceeds very slowly and, at molar ratios of reagents and catalyst 1 : 1 : 0.15; 1 : 1 : 0.3; 3 : 1 : 0.3, gives monobutyldiphenyls in yields of, respectively, 12, 14, and 18% of theory.

Experimental Part

The diphenyl required for the reaction was a commercial preparation with m.p. 70°. Pseudobutylene was isolated from the pseudobutylene-divinyl fraction from the manufacture of SK by polymerization of divinyl with metallic sodium. Before use it was purified from traces of isobutylene by passage through a column with 68% sulfuric acid and dried with calcium chloride.

The reaction was carried out analogously to the alkylation of benzene with pseudobutylene ([1]). At temperatures up to 70°, a solvent was used in the proportion of 200 ml of CCl_4 per mole of diphenyl. After introduction of the specified amounts of pseudobutylene, the reaction mixture was stirred at the same temperature for 2 hours and was left for some time at room temperature. Then the hydrocarbon layer was washed with water, with 5% solution

Table 1

Alkylation of diphenyl with pseudobutylene in the presence of $BF_3 \cdot H_3PO_4$

No. of experiment	Diphenyl, g	Pseudobutylene, g	$BF_3 \cdot H_3PO_4$ catalyst, g	Molar ratios of reactants and catalyst	Reaction temperature*, °C	Rate of pseudobutylene introduction, h	Monobutyldiphenyls obtained, g	Monobutyldiphenyls obtained, % of theory	b.p., °C (mm Hg)	n_D^4	d_4^{20}
1	38.50	16.27	6.21	1 : 1 : 0.15	65	3.5–4	7.59	12.3	119–129/2	1.5700	0.9748
2	154	58.3	33.20	1 : 1 : 0.2	70	5.5–6	101.4	46.4	124–142/3	1.5756	0.9730

No. of experiment	Diphenyl, g	Pseudodibutyl, g	$BF_3 \cdot H_3PO_4$, g	Molar ratios of reactants and catalyst	Reaction temperature*, °C	Rate of pseudobutylene introduction, h	Monobutyldiphenyls obtained, g	Monobutyldiphenyls obtained, % of theory	Monobutyldiphenyls b.p., °C (mm Hg)	n_D^4	d_4^{20}
3	38.48	14.92	8.31	1 : 1 : 0.2	90	4.5—5	24.79	47.2	136—143/3	1.5740	0.9724
4	38.50	16.97	12.47	1 : 1 : 0.3	55	4.5—5	9.00	14.2	113—128/2	1.5638	0.9618
5	38.56	8.29	4.18	1.75 : 1 : 0.13	90	2.5—3	10.10	32.5	139—146/3	1.5710	0.9741
6	38.50	8.27	6.20	1.75 : 1 : 0.25	50	1	4.62	15.0	108—119/1	1.5690	0.9734
7	38.57	8.19	6.21	1.75 : 1 : 0.25	90	2	17.78	57.9	126—143/3	1.5728	0.9736
8	38.86	8.73	8.33	1.75 : 1 : 0.3	90	2.5—3	19.42	59.3	121—140/3	1.5729	0.9738
9	154	30.00	16.60	2 : 1 : 0.2	90	5.5—6	43.56	38.8	152—162/8	1.5730	0.9709
10	38.50	6.45	6.20	2 : 1 : 0.3	100	1	9.10	37.6	135—148/3	1.5720	0.9646
11	38.56	7.07	8.31	2 : 1 : 0.4	90	2.5—3	10.09	38.4	160—182/9	1.5728	0.9758
12	58.00	7.38	6.21	3 : 1 : 0.3	60	2.5—3	5.07	18.3	141—154/7	1.5672	0.9682
13	58.07	7.27	6.23	3 : 1 : 0.3	90	2	6.4	23.5	158—160/8	1.5750	0.9768

No. of experiment	Diphenyl, g	Pseudobutylene, g	$BF_3 \cdot H_3PO_4$ catalyst, g	Molar ratios of reactants and catalyst	Reaction temperature*, °C	Rate of pseudobutylene introduction, h	Monobutyldiphenyls obtained, g	Monobutyldiphenyls obtained, % of theory	b.p., °C (mm Hg)	n_D^4	d_4^{20}
14	38.50	5.37	6.28	3 : 1 : 0.4	80	0.5—1	9.00	44.7	112—125/2	1.5672	0.9736
15	76.80	7.26	6.22	4 : 1 : 0.3	90	0.5—1	7.91	29.1	160—186/9	1.5713	0.9720

* Temperature fluctuations $\pm$2°.

of soda, again with water, dried with calcium chloride, and distilled. At atmospheric pressure the CCl_4 solvent evaporated, and the residue was distilled in vacuo from a Favorskii flask. In almost all experiments, a small amount of low-molecular olefin polymers distilled off at the beginning. The alkylation products were distilled into fractions boiling within ranges of 7 to 20° after preliminary separation of diphenyl. In the distillation flask there always remained from 0.1 to 1 g of a dark-brown viscous oil.

From the fractions corresponding to butyldiphenyls, on standing, *p*-tert-butyldiphenyl usually crystallized out; it was separated from liquid *p*-sec-butyldiphenyl by filtration.

To isolate pure products, the butyldiphenyl fractions from several experiments were combined and distilled on a rectification column with an efficiency of 20—25 theoretical plates. The relative content of secondary and tertiary butyldiphenyls in the mixture was determined by distilling the alkylate from specified experiments separately. In this case, *p*-tert-butyldiphenyl distilled within a range of 1° and crystallized immediately, and then, at the same temperature or 1—2° higher, *p*-sec-butyldiphenyl distilled. From polybutyldiphenyls it has not yet been possible to isolate definite products. The most characteristic experiments are summarized in Table 1.

n-sec-Butyldiphenyl is a colorless liquid, almost odorless. It contains traces of *n*-tert-butyldiphenyl. B.p. 117.5°/2 mm; d_4^{20} 0.9762; n_D^{20} 1.5718; MR_D 71.52, calculated 68.87.

Found, %: *M* 208.0; 213.2

$C_{16}H_{18}$. Calculated, %: *M* 210.1

Monobromide of *n*-sec-butyldiphenyl, obtained by bromination of the hydrocarbon in CCl_4 in the presence of iron filings, with a yield of 82%, consists of colorless crystals. After recrystallization from alcohol it has m.p. 98–99°.

Found, %: Br 27.93; 28.13

$C_{16}H_{17}Br$. Calculated, %: Br 27.66

Autoxidation of *n*-sec-butyldiphenyl. Into a glass column with a sealed-in Schott filter were placed 24.3 g (0.1 mole) of hydrocarbon, 0.4 mg of manganese resinate, and 14 mg of NaOH, and air was passed through the mixture for several hours at a rate of 0.1–0.2 l/min. Then 3% isopropylbenzene hydroperoxide was added, and the passage of air was continued. After 32 hours the concentration of hydroperoxide in the solution, determined iodometrically, reached 22%.

Decomposition of the hydroperoxide. To 0.1 g of BaO_2 and 3 drops of 79% H_2SO_4, at 0° and with continuous stirring, 10 g of 16.2% *n*-sec-butyldiphenyl hydroperoxide was added dropwise. Then an additional 3 drops of H_2SO_4 were introduced, and stirring was continued. In the process the mixture heated to 50°. On cooling to room temperature, an abundant precipitate separated from it. The reaction mass was treated with 10% NaOH solution; the alkaline solution was separated and acidified with hydrochloric acid. This gave 1.13 g, or 99.3% of the theoretical yield, of *n*-oxydiphenyl, which after two recrystallizations from benzene had m.p. 163–164°. Literature data ([2]): m.p. 164–165°. The methyl ether of the resulting *n*-oxydiphenyl had m.p. 87–88°. Literature data ([3]): m.p. 90°.

n-tert-Butyldiphenyl consists of colorless plates with m.p. 50–51.5° (from alcohol). Literature data ([4]): m.p. 52°. During distillation of the alkylate from a Favorskii flask, it distills over together with *n*-sec-butyldiphenyl in broad fractions and crystallizes from it on standing. On a rectification column with an efficiency of 20–25 theoretical plates, it distills at 112–113°/1 mm, at 146–147°/5 mm, and crystallizes immediately. A mixed sample of this product with *n*-tert-butyldiphenyl obtained by alkylation of diphenyl with isobutyl alcohol ([4]) gives no depression of the melting point.

Monobromide of *n*-tert-butyldiphenyl, obtained by bromination of the hydrocarbon in CCl_4 in the presence of iron filings, consists of colorless, odorless crystals with m.p. 132–133°.

Found, %: Br 27.85; 28.03

$C_{16}H_{17}Br$. Calculated, %: Br 27.66

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CITED LITERATURE

1. S. V. Zavgorodnii, L. S. Shvetsova, B. S. Khromykh, ZhOKh, **26**, 2180 (1956).

2. Beilstein, **6**, 1923, 674.

3. *Chemist' s Handbook*, **2**, 1951.

4. I. A. Roman, V. K. Berzinya, ZhOKh, **25**, 282 (1955).

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