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Abstract

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ARYLALKYLATION OF ANISOLE WITH STYRENE AND α-METHYLSTYRENE IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$ AND $BF_3 \cdot O(C_2H_5)_2$

(Presented by Academician A. V. Topchiev, 16 III 1961)

Arylalkylation of alkyl phenyl ethers with olefins has scarcely been studied. In the present work we investigated the reaction of anisole with styrene and α-methylstyrene in the presence of the catalysts $BF_3 \cdot H_3PO_4$ and $BF_3 \cdot O(C_2H_5)_2$. It has been shown that the reaction proceeds mainly according to the scheme:

$$CH_3O{-}C_6H_5 + CH_2{=}C(R){-}C_6H_5 \xrightarrow[\text{or } BF_3 \cdot O(C_2H_5)_2]{BF_3 \cdot H_3PO_4} CH_3O{-}C_6H_4{-}C(R)(CH_3){-}C_6H_5$$

$$(R = H \text{ or } CH_3).$$

When anisole is reacted with styrene in the presence of both catalysts, *p*-methoxydiphenylmethylmethane (I) is formed. The reaction is accompanied by partial polymerization of styrene. The most favorable conditions, under which (I) is formed in a yield of 87-88% of theory, are as follows: molar ratios of anisole, styrene, and catalyst, respectively, 5 : 1 : 0.3, and a temperature of 60°.

Anisole with α-methylstyrene forms *p*-methoxydiphenyldimethylmethane (II). The reaction proceeds less vigorously than with styrene. $BF_3 \cdot O(C_2H_5)_2$ proved to be the more effective catalyst in this reaction. In the presence of boron fluoride ethyl etherate, arylalkylation is accompanied to a lesser extent by polymerization and leads to the formation of a higher yield of (II). At molar ratios of anisole, α-methylstyrene, and $BF_3 \cdot O(C_2H_5)_2$ equal to 5 : 1 : 0.5, a temperature of 60°, and a time of 8.5 hr, the yield of (II) is 71% of theory. Lowering the temperature to 20–30° decreases the yield of (II) and intensifies the polymerization of α-methylstyrene into viscous resin-like products. In the presence of $BF_3 \cdot H_3PO_4$ the reaction is accompanied by more intensive polymerization of the olefin. In this case, along with viscous polymers, a dimer of α-methylstyrene is formed, namely 1,1,3-trimethyl-3-phenylindan. Under certain conditions (relatively small amounts of $BF_3 \cdot H_3PO_4$) the yield of this dimer is 46% based on α-methylstyrene. The best conditions, under which (II) is obtained in a yield of 55% of theory, are as follows: molar ratios of anisole, α-methylstyrene, and $BF_3 \cdot H_3PO_4$ 4 : 1 : 0.2, temperature 60°, and reaction time 1.5 hr.

The principal products of arylalkylation were identified by demethylation to the corresponding arylalkylphenols and conversion of the latter into arylalkylphenoxyacetic acids.

Experimental Part

Anisole was a freshly distilled commercial preparation with b.p. 154°, d_4^{20} 0.9908, n_D^{20} 1.5183. Styrene was a technical product; after fresh distillation it had b.p. 30°/3 mm, d_4^{20} 0.9047; n_D^{20} 1.5420. α-Methylstyrene was isolated from by-products of cumene phenol production; it had b.p. 35–40°/2 mm, d_4^{20} 0.9082; n_D^{20} 1.5360. The catalysts were prepared as before ([1]).

Arylalkylation of anisole with styrene. The reaction was carried out in a three-necked flask equipped with a stirrer, a thermometer, and a dropping funnel. Anisole and catalyst were placed in the flask, and, with vigorous stirring and at the specified temperature, styrene was added from the dropping funnel at a rate of 2.5–4 h/mole. For each experiment, 0.1–0.2 mole of styrene and the corresponding amounts of anisole and catalyst were taken. The reaction began after an induction period of 10–15 min and proceeded in a homogeneous medium, since the reactants, catalyst, and reaction products mixed well, forming a light-yellow liquid whose color did not change until the end of the reaction. After addition of the calculated amount of styrene, the reaction mixture was stirred for 1 h at the experimental temperature and worked up in the usual manner. The unreacted starting reagents were distilled off at atmospheric pressure. The reaction products were distilled in vacuo within a range of 3–5°. The resinous residue in the distillation flask amounted to 2–7 g. The most characteristic experiments are summarized in Table 1.

Table 1

Arylalkylation of anisole with styrene

No. of experiments	Molar ratio of anisole, styrene, and $BF_3 \cdot H_3PO_4$	Temp., °C $±$2°	Reaction duration	*n*-Methoxydiphenylmethylmethane, % of theoretical yield	Resinous residue in flask, g
1	5:1:0.3	60	1 h 45 min	88.2	5.3
2*	5:1:0.3	60	1 h 45 min	87.2	3.1
3	5:1:0.2	60	1 h 50 min	81.6	2.2

No. of experiments	Molar ratio of anisole, styrene, and $BF_3 \cdot H_3PO_4$	Temp., °C $\pm$2°	Reaction duration	n-Methoxydiphenylmethylmethane, % of theoretical yield	Resinous residue in flask, g
4	4:1:0.4	60	2 h	42.4	6.7
5	4:1:0.3	40	1 h 40 min	81.1	3.0
6	4:1:0.3	60	1 h 45 min	84.9	0.6
7*	4:1:0.3	60	1 h 45 min	70.7	4.3
8	4:1:0.2	40	1 h 45 min	79.7	2.3
9	4:1:0.2	60	1 h 50 min	81.1	4.4

* The experiments were carried out in the presence of the catalyst $BF_3 \cdot O(C_2H_5)_2$.

***n*-Methoxydiphenylmethylmethane (I)** is a transparent liquid; b.p. 161–163°/8 mm, d_4^{20} 1.0517; n_D^{20} 1.5735; MR_D 66.31; calculated 65.79. Literature data ([2]): b.p. 183°/17 mm, n_D^{26} 1.5680.

***n*-Oxydiphenylmethylmethane (III)** was obtained by demethylation of I. Fifteen grams of product I were mixed with 100 ml of HBr and 70 ml of acetic anhydride; the mixture was heated at gentle boiling for 45 h and worked up in the usual manner ([3]). On distillation, 5.5 g, or 39.2% of the theoretical yield of (III), was isolated. It is a viscous yellowish liquid. B.p. 133–134°/5 mm, d_4^{20} 1.1142; n_D^{20} 1.5885; MR_D 59.67; calculated 60.06. Literature data ([4]): b.p. 122–126°/1.5 mm, n_D^{23} 1.5904. From the demethylation products, in addition to (III), 0.5 g of phenol and small amounts of an unidentified hydrocarbon with b.p. 230°/4 mm, n_D^{20} 1.6011, were also isolated. Consequently, demethylation of I is accompanied by partial cleavage.

***n*-(α-Methylbenzyl)phenoxyacetic acid (IV).** Obtained from (III) and monochloroacetic acid in 83.7% of the theoretical yield.

ical. It consists of white plates. B.p. 97–99°. Molecular weight: found 256.7 and 259.0. $C_{16}H_{16}O_3$. Calculated 256.3.

Arylation-alkylation of anisole with α-methylstyrene. The reaction was carried out in the same way as with styrene. From the beginning to the end of the process the mixture was a homogeneous light-yellow liquid. When boron fluoride ethyl etherate was used, in some experiments anisole and α-methylstyrene were placed in the reaction flask, and the catalyst was added dropwise from a dropping funnel. For each experiment, 0.1 mole of α-methylstyrene and the corresponding amounts of anisole and catalyst were taken. The resinous residue in the distillation flask amounted to from 0.8 to 4.4 g. The arylalkylation product (II), even during the first rectification, distilled over within a range of 1–2°. In the reaction with the $BF_3 \cdot H_3PO_4$ complex, for each experiment 0.2 mole of α-methylstyrene and the corresponding amounts of anisole and catalyst were taken. In contrast to the catalyst boron fluoride ethyl etherate, in this case the arylalkylation is accompanied by intensive dimerization of α-methylstyrene to 1,1,3-trimethyl-3-phenylindan, which, during rectification of the alkylate, distills together with the main arylalkylation product, *p*-methoxydiphenyldimethylmethane, within a range of 2–5° and is separated from it by repeated freezing-out. In the distillation flask, as with the catalyst $BF_3 \cdot O(C_2H_5)_2$, a resinous viscous mass remains. Data from some experiments are summarized in Table 2.

Table 2

Arylation-alkylation of anisole with α-methylstyrene

Experiment No.	Molar ratio of anisole, α-methylstyrene, and catalyst	Temp., °C ±2°	Reaction duration, h	*p*-Methoxydiphenyldimethylmethane, % of theoretical	1,1,3-Trimethyl-3-phenylindan, % of theoretical	Resinous residue in flask, g
Catalyst $BF_3 \cdot O(C_2H_5)_2$*	**Catalyst** $BF_3 \cdot O(C_2H_5)_2$*	**Catalyst** $BF_3 \cdot O(C_2H_5)_2$*	**Catalyst** $BF_3 \cdot O(C_2H_5)_2$*	**Catalyst** $BF_3 \cdot O(C_2H_5)_2$*	**Catalyst** $BF_3 \cdot O(C_2H_5)_2$*	**Catalyst** $BF_3 \cdot O(C_2H_5)_2$*
1	7:1:0.5	40	8.0	62.4	Traces	0.8
2	5:1:0.5	40	6.5	67.7	”	1.0
3	5:1:0.5	60	8.5	70.8	”	0.8
4**	5:1:0.5	60	8.0	68.6	”	2.2
5	5:1:0.3	20	7.0	35.4	”	4.4
6	5:1:0.3	30	8.0	50.0	”	3.5
7	4:1:0.3	20	6.0	26.1	”	4.2
8	4:1:0.3	30	5.0	31.1	”	3.5
Catalyst $BF_3 \cdot H_3PO_4$	**Catalyst** $BF_3 \cdot H_3PO_4$	**Catalyst** $BF_3 \cdot H_3PO_4$	**Catalyst** $BF_3 \cdot H_3PO_4$	**Catalyst** $BF_3 \cdot H_3PO_4$	**Catalyst** $BF_3 \cdot H_3PO_4$	**Catalyst** $BF_3 \cdot H_3PO_4$
9	5:1:0.5	60	2.0	50.3	8.4	5.0
10	5:1:0.2	60	1.5	41.1	27.8	3.0
11	4:1:0.4	60	1.5	44.6	19.9	5.7
12	4:1:0.3	40	2.0	44.6	34.7	5.9
13	4:1:0.3	60	1.5	48.6	16.9	6.3
14	4:1:0.2	40	1.5	50.2	22.3	7.2
15	4:1:0.2	60	1.5	54.8	15.6	5.4
16	4:1:0.1	60	1.5	24.3	45.7	2.0
17	3:1:0.2	60	1.5	29.6	32.2	4.2
18	1:1:0.2	60	1.5	53.5	38.1	2.7

* A. I. Kosyakov participated in carrying out the experiment.
** In the experiment the catalyst was added dropwise to a mixture of anisole and α-methylstyrene.

***p*-Methoxydiphenyldimethylmethane (II)** is a colorless liquid with an anisole odor. It has b.p. 154-156°/3 mm, d_4^{20} 1.0424; n_D^{20} 1.5698; MR_D 70.89; calculated 71.52. Molecular weight: found 226.0. $C_{16}H_{18}O$. Calculated 226.1. Literature data (5): b.p. 198-199°/25 mm, d_4^{25} 1.0367; n_D^{25} 1.5685.

***p*-Oxydiphenyldimethylmethane (V)** was obtained by demethylation of II. 10 g of substance II were mixed with 100 ml of HBr and 70 ml of acetic anhydride and heated at gentle boiling for 45 h. After the corresponding

after treatment and distillation, 3 g, or 32.2% of the theoretical yield of V, was isolated; it consists of white crystals with m.p. 72-73°, which agrees with the literature data ([6]).

n-(α,α-Dimethylbenzyl)phenoxyacetic acid (VI). 1 g of substance V was dissolved in 5 ml of 33% NaOH solution; 1.5 g of monochloroacetic acid was added to the solution, and the mixture was heated for one hour on a water bath. After cooling to room temperature, the products were mixed with water, acidified, and extracted with ether. The ether extract was washed with 5% soda solution and acidified with HCl. The precipitated crystals of VI were filtered off and dried; the yield of VI was 0.7 g, or 55.1% of theory. M.p. 117-118° (from hot water). Literature data ([5]): m.p. 117°.

1,1,3-Trimethyl-3-phenylindan is obtained as white crystals. M.p. 53-54°. A mixed-melting test with the pure preparation gives no depression. Literature data ([7]): m.p. 52°.

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