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Abstract

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Alkylation of Aromatic Compounds with Diene Hydrocarbons

Alkenylation of Anisole with Piperylene

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Alkylation of the aromatic nucleus with diene hydrocarbons is a little-studied field, despite the availability of the starting materials. In most of the available papers and patents, the alkylation of divinyl is described (^{1}). Only one American patent (^{2}) reports the condensation of piperylene with toluene in the presence of $BF_3 \cdot H_3PO_4$. The use of piperylene in the synthesis of 4,7,8-trimethyl-2-ethyl-5-oxychroman is also mentioned (^{3}).

We undertook a systematic study of the reactions of alkylation of the aromatic nucleus with piperylene—a by-product of the production of synthetic rubber by the Lebedev method—in order to determine the reactivity of piperylene as a difunctional compound. Since piperylene contains two identical functional groups, it can react with an aromatic compound according to the general scheme (^{4}):

$$\mathrm{CH_3CH{=}CH{-}CH{=}CH_2} \xrightarrow{\mathrm{ArH}} \mathrm{CH_3CH(Ar){-}CH{=}CH{-}CH_3} \quad (V)$$

$$\mathrm{CH_3CH{=}CH{-}CH{=}CH_2} \xrightarrow{\mathrm{2ArH}} \mathrm{CH_3CH(Ar){-}CH(Ar){-}CH_2CH_3} \quad (VII)$$

$$\mathrm{CH_3CH(Ar){-}CH{=}CH{-}CH_3} \xrightarrow{\mathrm{ArH}} \mathrm{CH_3CH(Ar){-}CH(Ar){-}CH_2CH_3} \quad (VII)$$

where the course of the reaction in stages appears more probable. For the product containing a double bond, 6 isomers are theoretically possible:

$\mathrm{CH_3CH{=}CH{-}CH(Ar)CH_3}$ (*I*)
$\mathrm{CH_3CH{=}CH{-}CH_2CH_2Ar}$ (*II*)
$\mathrm{CH_3CH(Ar)CH_2CH{=}CH_2}$ (*III*)
$\mathrm{CH_3CH_2CH(Ar)CH{=}CH_2}$ (*IV*)
$\mathrm{CH_3CH_2CH{=}CH{-}CH_2Ar}$ (*VI*)

As is evident, the products of addition of one molecule of an aromatic compound to piperylene in positions 1,2 (*I*) and 1,4 (*V*) have the same structure. As a diene hydrocarbon, piperylene in alkylation should more likely give the product of addition in position 1,4 (*V*), in accordance with the distribution of electron density in the molecule ([5]). However, in the literature ([2],[3]) products (*VI*) are described, formed by addition of the aromatic compound in positions 1,4, but contrary to Markovnikov' s rule (the phenyl radical is attached to the primary carbon atom). For substituted benzenes, different orientations of the pentenyl group are also possible, and among the high-boiling products, along with compounds of the diarylpentane series (*VII*), polypentenylbenzenes ([6]) may occur. Thus, as a result of the reaction one could expect a complex mixture of substances.

In the present work, using anisole as an example, the possibility of alkenylation of the aromatic nucleus with piperylene is shown, with yields of pentenylanisoles

56–92% of theory. Anisole was chosen as the first object of study as a representative of substances containing sufficiently mobile hydrogens, in order to avoid the use of vigorous catalysts and thereby eliminate the polymerization of piperylene. Molecular compounds of boron fluoride were tested as catalysts: $BF_3 \cdot O(C_2H_5)_2$, $BF_3 \cdot H_3PO_4$, BF_3, 100% H_3PO_4; for comparison—conc. H_2SO_4, $AlCl_3$, $AlCl_2 \cdot H_2PO_4$ (7). With all these catalysts the alkylation process suppresses the polymerization of piperylene.

Table 1

Alkylation of anisole with piperylene

Experiment No.	Catalyst	Molar ratio piperylene:anisole:catalyst	Addition time	Standing time	Pentenylanisole fraction: b.p., °C/mm	Pentenylanisole fraction: yield, % of theory	Pentenylanisole fraction: n_D^{20}	High-boiling products: boiling limits, °C/mm	High-boiling products: residue in flask, g	High-boiling products: %**
1	$BF_3 \cdot O(C_2H_5)_2$	1:1:0.10	10 h 45 min	40 h 00 min	109–120/5	25.8	1.5153	120–230/5	2.20	59.9
2	Same	1:3.7:0.30	12 h 45 min	44 h 00 min	114–116/9	12.2	1.5183	–	1.00	33.7

Experiment No.	Catalyst	Molar ratio piperylene:anisole:catalyst	Addition time	Standing time	Pentenylanisole fraction: b.p., °C/mm	Pentenylanisole fraction: yield, % of theory	Pentenylanisole fraction: n_D^{20}	High-boiling products: boiling limits, °C/mm	High-boiling products: residue in flask, g	High-boiling products: %**
3	Same	1:3.7:0.03	9 h 10 min	64 h 30 min	90–96/2	19.5	1.5189	110–138/2	1.80	36.9
4	Same	1:3.7:0.06	6 h 20 min	46 h 00 min	109–111/7	53.7	1.5176	140–185/7	1.80	2.5
5	Same	1:3.7:0.10	3 h 30 min	104 h 30 min***	89–96/2.5	25.8	1.5175	98–220/2.5	0.95	73.2
6	Same	1:3.6:0.10	1 h 00 min	19 h 00 min	94–95/2	44.3	1.5180	120–143	2.3	35.0
7	Same	1:3.7:0.11	3 h 40 min	46 h 00 min	94–97/2	56.8	1.5180	100–180/2	0.65	22.8
8	Same	1:3.7:0.20	9 h 00 min	42 h 30 min	87–90/1.5	57.2	1.5191	123–210/1.5	0.57	31.5
9	Same	1:3.7:0.25	5 h 20 min	45 h 30 min	94–100/3	58.8	1.5176	140–200/3	0.74	30.3
10	Same	1:10:0.25	10 h 20 min	47 h 30 min	99–102/3.5	62.4	1.5112	120–215/3.5	1.07	0.0
11	Same	1:3.7:0.30	9 h 00 min	41 h 00 min	87–90/1.5	57.5	1.5180	125–210/2	0.58	31.7

Experiment No.	Catalyst	Molar ratio piperylene:anisole:catalyst	Addition time	Standing time	Pentenylanisole fraction: b.p., °C/mm	Pentenylanisole fraction: yield, % of theory	Pentenylanisole fraction: n_D^{20}	High-boiling products: boiling limits, °C/mm	High-boiling products: residue in flask, g	High-boiling products: %**
12	Same	1:3.7:0.40	1 h 40 min	48 h 00 min	101–110/5	51.8	1.5171	145–200/5–8	0.70	33.9
13	Same	1:3.7:0.30	6 h 10 min	48 h 00 min	90–100/2.5	45.1	1.5180	125–180/2	1.38	41.3
14	100% H_3PO_4	1:4:0.25	13 h 30 min	36 h 30 min	95–100/2.5	2.2	1.5197	110–145/2.5	0.74	8.6
15	Same	1:5:0.25	9 h 00 min	–	95–105/3.5	88.5	1.5181	110–140/3	1.26	7.5
16	85% H_3PO_4	1:4:0.25	8 h 00 min	–	96–108/5	44.7	1.5186	–	0.7	9.5
17	96% H_2SO_4	1:5:0.25	9 h 00 min	–	95–102/2.5	71.3	1.5179	120–200/2.5	0.82	21.7
18	$BF_3 \cdot H_3PO_4$	1:4:0.10	8 h 10 min	–	96–106/4	65.4	1.5190	140–165/4	1.28	22.5
19	Same	1:10:0.10	8 h 10 min	–	97–100/3	55.1	1.5198	110–210/3	0.37	16.8
20	Same	1:10:0.25	7 h 00 min	9 h 00 min	95–105/3.5	84.0	1.5182	130–195/3.5	0.64	13.9
21	$AlCl_2 \cdot H_2PO_4$	1:4:0.10	5 h 30 min	–	94–100/2.5	65.7	1.5188	120–148/2.5	0.67	27.1
22	BF_3	1:4:0.10	1 h 30 min	–	101–110/3	65.4	1.5172	128–187/3	1.16	26.7

Experiment No.	Catalyst	Molar ratio piperylene:anisole:catalyst	Addition time	Standing time	Pentenylanisole fraction: b.p., °C/mm	Pentenylanisole fraction: yield, % of theory	Pentenylanisole fraction: n_D^{20}	High-boiling products: boiling limits, °C/mm	High-boiling products: residue in flask, g	High-boiling products: %**
23	Same	1:4:0.12	5 h 00 min	41 h 00 min	78–90/2	27.8	1.5120	103–240/2****	2.90	69.1
24	$AlCl_3$	1:4:0.07	2 h 30 min	–	85–105/3	65.4	1.5180	134–190/3	1.00	25.9

* Amount of piperylene in all experiments: 6.81 g (0.1 mole).

** Amount of high-boiling products, including the residue during distillation, as % of the sum of the substances obtained.

*** After 10 h standing, heating for 2 h on a boiling water bath.

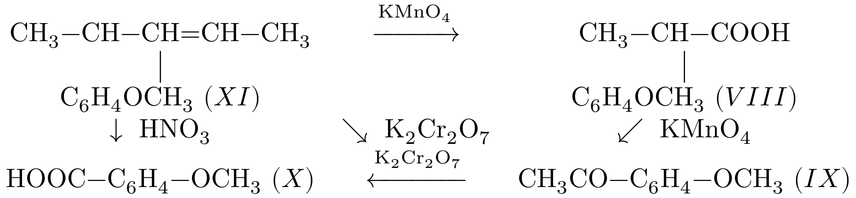
**** From the fraction 180–260° at 2 mm and n_D^{20} 1.5537, on standing, crystals precipitate with m.p. 106–107.5° (from alcohol), corresponding by m.p. to 2,3-bis-(p-methoxyphenyl)-pentane.

The results of part of a large series of experiments are presented in Table 1. Alkylation is best carried out with cooling and continuous mechanical stirring by gradually adding piperylene, diluted with an equal volume of anisole, to a mixture of anisole and catalyst at such a rate that the temperature of the reaction mixture does not rise above 10–20°. After the addition of piperylene is complete, stirring is continued at room temperature. For the solid catalysts $AlCl_3$ and $AlCl_2 \cdot H_2PO_4$ the reverse order of addition of reagents was used: the catalyst was added to a mixture of anisole and piperylene. Heating usually increases the overall yield of reaction products, but at the expense of formation of high-boiling substances. Dilution of the reaction mixture with an excess of anisole up to 3.5–5 moles per mole of piperylene, as well as the duration of the reaction, has a great influence on the yield of pentenylanisoles. With boron fluoride ethyl etherate, in order to obtain good yields of pentenylanisole, the reaction mixture must be left at room temperature for 40–45 h. With more vigorous catalysts—$BF_3 \cdot H_3PO_4$, $AlCl_2 \cdot H_2PO_4$, BF_3, $AlCl_3$—good yields are obtained under the same conditions with contact of the rea-

reagents for no more than 2–8 hr. Increasing the duration of the reaction in the presence of these catalysts promotes the accumulation of high-boiling products;

for example, with BF_3 it is possible to isolate 2,4-bis-(p-methoxyphenyl)pentane.

Proof of the structure of the pentenylanisoles was carried out by oxidation at the double bond for the product obtained with boron fluoride etherate. According to the scheme, oxidation with $KMnO_4$ in acetone solution gave, in good yields, p-methoxyhydratropic acid (VIII) and p-methoxyacetophenone (IX):



$$\begin{array}{ccc} CH_3-\underset{\displaystyle C_6H_4OCH_3\ (XI)}{\underset{|}{CH}}-CH{=}CH-CH_3 & \xrightarrow{KMnO_4} & CH_3-\underset{\displaystyle C_6H_4OCH_3\ (VIII)}{\underset{|}{CH}}-COOH \\ \downarrow HNO_3 & \searrow K_2Cr_2O_7 & \swarrow KMnO_4 \\ HOOC-C_6H_4-OCH_3\ (X) & \xleftarrow{K_2Cr_2O_7} & CH_3CO-C_6H_4-OCH_3\ (IX) \end{array}$$

Oxidation with chromic mixture gives a mixture of p-methoxyacetophenone and anisic acid (X). Anisic acid was also obtained on oxidation with 25% nitric acid. The formation of p-methoxyacetophenone unquestionably indicates the position of the anisole residue at the second carbon atom, and the formation of p-methoxyhydratropic acid indicates the β-position of the double bond. On this basis it may be concluded that the pentenylanisole obtained in the presence of $BF_3 \cdot O(C_2H_5)_2$ consists, in its main mass, of 4-(p-methoxyphenyl)pentene-2 (XI), which is mentioned in the literature as an intermediate product in the synthesis of 2,3-bis-(p-hydroxyphenyl)pentane ([8]), and, consequently, the addition of anisole to piperylene proceeds in accordance with its polarity ((I) or (V)).

The products obtained in alkylation in the presence of BF_3, H_3PO_4, and $BF_3 \cdot H_3PO_4$ also, apparently, consist mainly of 4-(p-methoxyphenyl)pentene-2. This is indicated by the closeness of the constants and by the fact that, on further interaction of pentenylanisole with anisole, crystalline 2,3-bis-(p-methoxyphenyl)pentane is formed both in the reaction itself (with BF_3) and when the synthesis is carried out in two stages.

Experimental Part

The alkylation was carried out in the usual manner, as described in the theoretical part. Piperylene was used with b.p. 41-42.5°, n_D^{20} 1.4245, d_4^{20} 0.6795. By distillation on a column of the pentenylanisoles obtained in experiments with $BF_3 \cdot O(C_2H_5)_2$, two principal fractions were isolated.

1st fraction. B.p. 86.5-87.0°, at 1 mm, n_D^{20} 1.5178, d_D^{20} 0.9513, MR 56.12, calc. 55.19.

Found, %: C 81.58; 81.40; H 8.91; 9.05
$C_{12}H_{16}O$. Calculated, %: C 81.77; H 9.16

2nd fraction. B.p. 88-88.2°, at 1.5 mm, n_D^{20} 1.5182, d_4^{20} 0.9513, MR 56.15, calc. 55.19.

Found, %: C 81.61; 81.87; H 9.40; 9.56
$C_{12}H_{16}O$. Calculated, %: C 81.77; H 9.16

Both fractions are colorless, readily mobile liquids with a peculiar odor and give the same products on oxidation with $KMnO_4$.

Oxidation of pentenylanisole. a. On oxidation of 5.23 g (0.03 mole) of fraction 1, dissolved in 125 ml of acetone and 10 ml of water, perman-

with potassium permanganate gave 2.03 g (42.3% of theory) of *p*-methoxyhydratropic acid (9) with m.p. 46–47° (from a mixture of ether and petroleum ether). Distillation of the oil (2.05 g) isolated from the neutral portion gives 1.04 g of a fraction with b.p. 100-130° at 3-4 mm, n_D^{20} 1.5353, and 0.6 g of a fraction with b.p. 130-150° at 3-4 mm, n_D^{20} 1.5364. The 2,4-dinitrophenylhydrazone obtained from the corresponding fractions melts at 219-220° and 218-219° (from xylene), which corresponds to the m.p. of the 2,4-dinitrophenylhydrazone of *p*-methoxyacetophenone (10). The m.p. of a mixed sample with the 2,4-dinitrophenylhydrazone of *p*-methoxyacetophenone obtained from anisole and acetic anhydride (11) shows no depression. The yield of *p*-methoxyacetophenone is 44.3% of theory.

b. Fraction 2, when oxidized under the same conditions but in dry acetone, gives 1.85 g (38.3%) of *p*-methoxyhydratropic acid with m.p. 56-57° (from a mixture of ether and petroleum ether) and 2.08 g (46.4%) of *p*-methoxyacetophenone, the 2,4-dinitrophenylhydrazone of which melts at 218-219° (from xylene). The m.p. of a mixed sample with a synthetic specimen shows no depression.

c. From 1.76 g (0.01 mole) of fraction 1, upon oxidation with 8.9 g of $K_2Cr_2O_7$, 35.2 ml of water, and 9.6 ml of conc. H_2SO_4, by heating for 3 hr, 0.7 g (46.6%) of *p*-methoxyacetophenone was obtained; m.p. of the 2,4-dinitrophenylhydrazone 211-212° and of a mixed sample with a synthetic specimen 214-215°. From the acidic portion, anisic acid with m.p. 182° was isolated in insignificant amount (literature m.p. 184° (9)).

d. Oxidation of 1 g of fraction 1 with 75 ml of 25% HNO_3 gives anisic acid with m.p. 182-184° (after sublimation and repeated crystallization from water and alcohol).

Alkylation of anisole with pentenylanisole in the presence of $BF_3 \cdot H_3PO_4$. From 19.08 g (0.1 mole) of pentenylanisole obtained with H_3PO_4, 23.3 g (0.22 mole) of anisole, and 3.58 g (0.02 mole) of $BF_3 \cdot H_3PO_4$, upon heating on a water bath and stirring for 2 hr, 10.25 g (33.4%) of a dianisylpentane fraction was obtained, with b.p. 190-207° at 8 mm, d_4^{20} 1.0590, n_D^{20} 1.5610, MR 86.76, calculated 86.03. Upon addition of absolute alcohol and freezing, the substance crystallizes almost completely, m.p. 106-107.0° (from alcohol). Literature data (8) for 2,3-bis-(*p*-methoxyphenyl)pentane: m.p. 106-108°.

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