V. D. RYABOV, V. L. VAISER, CHZHU YUI-TUN

1962

SovietRxiv

Abstract

Full Text

Chemistry

V. D. RYABOV, V. L. VAISER, CHZHU YUI-TUN

INTERACTION OF TOLUENE WITH PHENYLACETYLENE

(Presented by Academician A. V. Topchiev, 16 IV 1962)

Previously we studied in detail the alkylation reaction of aromatic hydrocarbons of the benzene and naphthalene series, phenols, naphthols, phenol ethers, and other compounds with acetylene in the presence of boron fluoride compounds ([1]), and, in development of these works, since 1959 investigations were begun on the interaction of aromatic compounds with acetylene homologs. We showed ([2]) that, in the alkylation of phenol with methylacetylene in the presence of catalysts based on boron fluoride, 2,2-bis-(oxyphenyl)-propane is obtained in good yield; this is a valuable intermediate for the preparation of epoxy and polycarbonate resins.

In the present work the results are reported of a study of the interaction of toluene with phenylacetylene. Proceeding from the well-studied regularities of the reaction between aromatic compounds and acetylene, we assumed that, in the case of the reaction of toluene with phenylacetylene, 1-phenyl-1-tolylethylene (I) and 1-phenyl-1,1-ditolylethane (II) would be formed:

$$CH_3{-}C_6H_5 + HC{\equiv}C{-}C_6H_5 \longrightarrow CH_3{-}C_6H_4{-}C(=CH_2){-}C_6H_5 \qquad (I)$$

$$CH_3{-}C_6H_4{-}C(=CH_2){-}C_6H_5 + C_6H_5{-}CH_3 \longrightarrow CH_3{-}C_6H_4{-}C(CH_3)(C_6H_5){-}C_6H_4{-}CH_3 \qquad (II)$$

The experiments were carried out in a three-necked flask equipped with a stirrer with a seal, a thermometer, and a dropping funnel.

In the first series of preliminary experiments a number of reaction catalysts was investigated: sulfuric acid (1.83), an aluminosilicate catalyst*, molecular compounds of boron fluoride with orthophosphoric acid and with diethyl ether. In some experiments mercury oxide was added to the catalysts. It is known that acetylene enters into reaction only in the presence of special additives to an acid catalyst; these additives (usually mercury salts) play the role of activators of the triple bond of acetylene, the molecule of which is capable of being activated under the influence of coordinatively unsaturated atoms. Unsymmetrical homologs of acetylene are polarized and are characterized by increased reactivity.

In this connection it was to be expected that phenylacetylene would enter into reaction even without activating additives. Experimental verification confirmed this assumption.

The experiments were carried out as follows. Toluene was placed in the flask (b.p. 108–110°; n_D^{20} 1.4968), catalyst, and from the dropping funnel add-

* A tableted aluminosilicate catalyst in the form of a fraction obtained by sieving through a 100-mesh sieve; before the experiment it was subjected to thermal treatment for 2 hours at 500°.

was 50 g of a 20% solution of phenylacetylene* (b.p. 141–142°; n_D^{15} 1.5503) in toluene. After the addition of the solution of phenylacetylene in toluene, the reaction mixture was stirred for some time. The reaction products were washed to neutral reaction, dried with calcium chloride, and the unreacted toluene was distilled off; the residue was subjected to vacuum distillation. As a result of vacuum distillation at 5–6 mm Hg, fractions were obtained: 120–146° and 210–250°. In some cases a low-boiling fraction, 86–120°, was obtained. As investigation of this fraction showed, it consisted of 1-phenyl-1-tolylethylene mixed with a small amount of acetophenone. Acetophenone was isolated by distillation as the fraction 118–211° (n_D^{20} 1.5391) and identified by preparation of the semicarbazone, m.p. 198.6°. 1-Phenyl-1-tolylethylene was isolated from the mixture of the 86–120° and 120–146° fractions as an oily, slightly fluorescent liquid: b.p. 127–129° at 5 mm Hg, n_D^{20} 1.5931, d_4^{20} 1.0037; mol. wt. 194.4, 194; calculated 196.

Found, %: C 92.30, 92.46; H 7.53, 7.38
Calculated, %: C 92.78; H 7.22

1-Phenyl-1-tolylethylene was reduced (sodium, alcohol); as a result, 1-phenyl-1-tolylethane was obtained; b.p. 126–127° at 4 mm Hg: n_D^{20} 1.5685; d_4^{20} 0.9940; MR found 64.4; calculated 64.3. Literature data for 1-phenyl-1-tolylethane (4): n_D^{20} 1.5680; d_4^{20} 0.9885. The bulk of the 1-phenyl-1-tolylethylene was contained in the 120–146° fraction.

Investigation of the mixture of the 210–250° fractions showed that the main product contained in this fraction is 1,1-ditolyl-1-phenylethane, which is a transparent glassy substance of pale-yellow color: b.p. 219–229° at 4 mm Hg; mol. wt. 287, 286.2; calculated 286; MR found 93; calculated 93.04:

Found, %: C 92.32, 92.58; H 7.57, 7.58
Calculated, %: C 92.3; H 7.7

In studying the influence of various catalysts, the best results were obtained when a molecular compound of orthophosphoric acid with boron fluoride was used. The reaction did not proceed in the presence of boron fluoride etherate. In the presence of sulfuric acid and an aluminosilicate catalyst, reaction products containing appreciable amounts of acetophenone were obtained. Evidently, phenylacetylene was partially hydrated at the expense of the water contained in the sulfuric acid or adsorbed by the aluminosilicate catalyst.

The yields of 1-phenyl-1-tolylethylene and 1-phenyl-1,1-ditolylethane in the presence of sulfuric acid and the aluminosilicate catalyst are approximately the same and 3–4 times lower than when a molecular compound of phosphoric acid and boron fluoride is used.

The influence of a number of factors on the yield and composition of the reaction products was investigated: the influence of the amount of catalyst, temperature, the molar ratio toluene : phenylacetylene, and the duration of the reaction after mixing of the reagents. To study the influence of catalyst concentration, experiments were carried out in the presence of 2.5; 10; and 15 ml of the molecular compound of orthophosphoric acid with boron fluoride, which amounted, respectively, to 1.24; 3.1; 6.3; 9.3% by volume of the toluene taken for the reaction. The molar ratio toluene : phenylacetylene in all experiments was 15 : 1. The temperature was 60°. 50 g of a 20% solution of phenylacetylene in toluene was fed to a mixture of 100 g of toluene and catalyst at a rate of 1 drop per second, after which the reaction mixture was stirred for 1 hour. The results of the experiments are given in Table 1.

* Phenylacetylene was obtained by dehydrobromination of styrene dibromide (3).

With an increase in the amount of catalyst, the yield of tolylphenylacetylene decreases, while the yield of phenylditolylethane increases along with an increase in the yield of resinous products.

Table 1

Effect of the amount of catalyst on the reaction of toluene with phenylacetylene

No.	Amount of catalyst, % of toluene	Yield*, %: phenyltolylacetylene	Yield*, %: phenylditolylethane	Resins**, %
1	1.24	37.4	18.5	1.6
2	3.1	29.5	26.3	1.7
3	6.3	28.6	29	1.8
4	9.3	26.7	29.5	1.82

* Yield as percent of theoretical, calculated for phenylacetylene.
** Residue in the distillation flask, as percent of the weight of phenylacetylene.

In order to determine the effect of temperature on the yield and composition of the reaction products, experiments were carried out at 5, 20, 60, and 90°; the amount of catalyst in all experiments was 6.3% by volume of the toluene taken into the reaction, and the remaining reaction conditions were the same as in the preceding experiments on the effect of the amount of catalyst. The results of the experiments are given in Table 2.

Table 2

Effect of temperature on the reaction of toluene with phenylacetylene

No.	Temp., °C	Yield, %: phenyltoly-lacetylene	Yield, %: phenylditolylethane	Resins, %
1	5	23	22.8	2.8
2	20	29	27	1.8
3	60	28.6	29.0	1.8
4	90	28.3	33.1	1.1

With an increase in temperature, the yield of the reaction products increases, and the yield of phenylditolylethane increases more rapidly; with an increase in temperature, resin formation decreases.

Table 3

Effect of the molar ratio toluene : phenylacetylene

No.	Mol. ratio	Yield, %: phenyltoly-lacetylene	Yield, %: phenylditolylethane	Resins, %
1	3:1	21.3	22.4	2.5
2	6:1	22.9	28	2.2
3	10:1	26.5	29.5	2.2
4	15:1	28.6	29.0	1.8

Table 3 gives data illustrating the effect of the molar ratio toluene : phenylacetylene; the experiments were carried out at various molar ratios at a temperature of 60°; the amount of catalyst was 6.3% of toluene.

With an increase in the molar ratio, the yields of the reaction products increase, and resin formation decreases. The optimum molar ratio is 10 : 1.

With an increase in the duration of the reaction (Table 4) after mixing the reagents from 10 to 180 min, other conditions being equal (temperature 60°; molar ratio 15 : 1), the yield of phenyltolylethylene decreases, while the yield of phenylditolylethane increases, together with a certain increase in resin formation.

Table 4

Effect of reaction duration

No.	Reaction duration, min	Yield, %: phenyl-tolylethylene	Yield, %: phenylditolylethane	Resins, %
1	10	30.2	26.7	1.63
2	60	28.6	29	1.78
3	120	26.2	30.2	1.7
4	180	25.8	31.2	1.96

The results of all the experiments on the influence of the above-listed factors confirm our initial assumption that the reaction of toluene with phenylacetylene proceeds by a consecutive mechanism, with formation of 1-phenyl-1-tolylethylene as an intermediate compound.

Favorable conditions for the formation of 1-phenyl-1-tolylethylene are: temperature 20–30°, reaction duration after addition of the reagents not more than 10 min, and an amount of catalyst up to 1% of the toluene taken into the reaction.

The formation of 1-phenyl-1,1-ditolylethane is favored by increased catalyst concentrations, $\sim 9\%$, a temperature of 90–100°, and an increased contact time of the reagents with the catalyst (up to 2 h). The reaction should be carried out with a large excess of toluene, which is necessary for suppressing side processes.

Institute of Petrochemical
and Gas Industry
named after I. M. Gubkin

Received
16 IV 1962

CITED LITERATURE

1. V. L. Vaisser, *Alkylation of Organic Compounds with Acetylene*, doctoral dissertation, 1959.
2. V. D. Ryabov, V. L. Vaisser, Author' s Certificate No. 143812.
3. N. Fiesselmann, K. Sasse, *Chem. Ber.*, **89**, 1786 (1956).
4. A. Petrova, O. Shvarts, ZhOKh, **20**, 2168 (1950).

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