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Abstract

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CONDENSATION OF ALKYLBENZENES WITH HALOGEN DERIVATIVES OF ISOBUTYLENE

The reaction of alkylation of aromatic hydrocarbons by alkenyl halides using sulfuric acid as a catalyst is of undoubted interest, since it makes it possible to obtain alkyl-aromatic compounds containing a halogen atom in the alkyl radical by a simple route. It has been established ([1]) that allyl chloride, like propylene, condenses with benzene in the presence of sulfuric acid at the expense of the double bond; in this process β-chloroisopropylbenzene is obtained. Later, methallyl chloride was used as a chloroalkylating agent, and hydrogen fluoride ([2]) and sulfuric acid ([3]) as catalysts. With a ratio benzene : methallyl chloride : 96% sulfuric acid of 3 : 1 : 0.15, the yield of β-chloro-tert-butylbenzene was 68%. Even after changing the ratio of reagents to 3.3 : 3.8 : 3.9, Shmerling and Ipatieff ([4]) obtained mainly β-chloro-tert-butylbenzene and bis-(β-chloro-tert-butyl)-benzene in a yield of only 2.6%. In the chloroalkylation of toluene with isocrotyl chloride, a product was obtained to which, without any proof, the structure of n-(β-chloro-tert-butyl)toluene was assigned ([5]). Having set ourselves the task of synthesizing alkyl-aromatic hydrocarbons and their derivatives with branched alkyl radicals containing quaternary carbon atoms, we carried out the condensation of methallyl chloride with alkylbenzenes:

$$C_6H_5R + CH = C(CH_3)CH_2Cl \xrightarrow{H_2SO_4} R - C_6H_4C(CH_3)_2CH_2Cl,$$

where R : CH_3—, C_2H_5—, iso-C_3H_7—, tert-C_4H_9 and $(CH_3)_3C$—CH_2—.

The conditions under which the condensation reactions were carried out, the ratios of the reagents, and the yields of products are presented in Table 1; the properties of the substances obtained are given in Table 2. In all cases, condensation products were obtained in yields of 64–98%, which, as can be seen from Table 1 in the example of tert-butylbenzene, depend on the order in which the reagents are added. In the case when the acid was added to a mixture of tert-butylbenzene and methallyl chloride (all other conditions being equal), the yield was 42%; if methallyl chloride was added to a mixture of tert-butylbenzene

and sulfuric acid, it was 64%. The amount of sulfuric acid and the reaction temperature also exert a substantial influence. When the ratio methallyl chloride : sulfuric acid was changed from 1 : 0.15 to 1 : 0.5 and the temperature was lowered from 20 to 0°, the yield increased from 64% to 98%. Only from the products of the reaction of tert-butylbenzene with methallyl chloride was it possible to isolate *n*-(*β*-chloro-tert-butyl)tert-butylbenzene, which is a solid substance readily crystallizing from a mixture with the meta isomer. The liquid residue and all the other (*β*-chloro-tert-butyl)alkylbenzenes, as analysis of the infrared spectra showed, are mixtures of *p*- and *m*-isomers, which could not be separated either by distillation on a column or by freezing out. Attempts were made to determine the ratio of isomers in the condensation products of methyl-, ethyl-,

Table 1

Starting substances	Ratio of alkylbenzene : haloalkylene : H_2SO_4	Reaction temp., °C	H_2SO_4 concentration, %	Reaction product	Yield, %
C_6H_6 and $H_2C{=}C(CH_3)CH_2Cl$	3 : 1 : 0.15	20	96	$C_6H_5{-}C(CH_3)_2CH_2Cl$n-$ClCH_2C(CH_3)_2C_6H_4{-}C(CH_3)_2CH_2Cl$with an admixture of the *m*-isomer	64–662–4
Same	3 : 1 : 0.15	0–4	100	$C_6H_5C(CH_3)_2CH_2Cl$n-$ClCH_2C(CH_3)_2{-}C_6H_4{-}C(CH_3)_2CH_2Cl$with an admixture of the *m*-isomer	72–74
""	3 : 1 : 0.5	20	96	$C_6H_5{-}C(CH_3)_2CH_2Cl$n-$ClCH_2C(CH_3)_2C_6H_4C(CH_3)_2{-}CH_2Cl$with an admixture of the *m*-isomer	6012

Starting substances	Ratio of alkylbenzene : haloalkylene : H_2SO_4	Reaction temp., °C	H_2SO_4 concentration, %	Reaction product	Yield, %
C_6H_6 and $BrCH{=}C(CH_3)_2$	3 : 1 : 0.15	20	100	$C_6H_5{-}C(CH_3)_2CH_2Br$	23.5
Same	3.4 : 1 : 0.26	20	100	Same	35
C_6H_6 and $CH_2{=}C(CH_2Cl)_2$	3 : 1 : 1	20	96	–	–
Same	3 : 1 : 1	20	100	$C_6H_5C(CH_2Cl)_2{-}CH_3$	3.6
""	1.5 : 1 : 1	50–60	100	Same	3
""	3.8 : 1 : 1	30	100	""	6.3
$CH_3{-}C_6H_5$ and $H_2C{=}C(CH_3)CH_2Cl$	3 : 1 : 0.15	20	100	n-$CH_3{-}C_6H_4{-}C(CH_3)_2CH_2Cl$ with an admixture of the *m*-isomer	74.5
$C_2H_5{-}C_6H_5$ and $H_2C{=}C(CH_3){-}CH_2Cl$	3 : 1 : 0.15	10	100	n-$C_2H_5{-}C_6H_4{-}C(CH_3)_2CH_2Cl$ with an admixture of the *m*-isomer	73
n-$C_3H_7{-}C_6H_5$ and $H_2C{=}C(CH_3){-}CH_2Cl$	3 : 1 : 0.15	10	100	n-n-$C_3H_7{-}C_6H_4{-}C(CH_3)_2CH_2Cl$ with an admixture of the *m*-isomer	70
Same	3 : 1 : 0.3	10	100	Same	80
""	3 : 1 : 0.5	0	100	""	65.5

Starting substances	Ratio of alkylbenzene : haloalkylene : H_2SO_4	Reaction temp., °C	H_2SO_4 concentration, %	Reaction product	Yield, %
tert-C_4H_9–C_6H_5 and H_2C=C(CH_3)CH_2Cl	3 : 1 : 0.15	20	100	n-tert-C_4H_9–C_6H_4–$C(CH_3)_2$–CH_2Clwith an admixture of the *m*-isomer	64
Same*	3 : 1 : 0.15	20	100	Same	42
””	3 : 1 : 0.3	10	100	””	70.5
””	3 : 1 : 0.6	10	100	””	65.5
””	3 : 1 : 0.5	0	100	””	98–99
tert-C_4H_9–C_6H_5 and BrCH=C(CH_3)$_2$	1.5 : 1 : 0.15	20	100	n-tert-C_4H_9–C_6H_4–$C(CH_3)_2CH_2$Br	23.5
C_5H_{11}–C_6H_5 + H_2C=C(CH_3)–CH_2Cl	3 : 1 : 0.5	30	96	n-C_5H_{11}–C_6H_4–$C(CH_3)_2CH_2$Cl	14
Same	3 : 1 : 0.5	20	96	Same	54

* The acid was added in portions of 10 g to the mixture of tert-butylbenzene and methallyl chloride over one hour.

Isopropyl- and tert-butylbenzene with methallyl chloride were determined by oxidizing them with nitric acid and separating the resulting phthalic acids in the form of their barium salts ([6]). However, in all cases it was possible to isolate only terephthalic acid. On the basis of the oxidation data presented in the experimental part, it may be assumed that the *m*-isomers are formed in very small amounts, while the principal products are the *p*-isomers. To clarify the question of the relative reactivity in the condensation reaction of alkylbenzenes and benzene, an experiment was carried out on chloroalkylation of an equimolecular mixture of benzene and cumene with methallyl chloride. It turned out that the reaction products contain approximately equal amounts of *β*-chloro-tert-butylbenzene and *β*-chloro-tert-butylcumene. In order to broaden

the range of haloalkylating agents, the condensation reactions of benzene and tert-butylbenzene with bromoisocrotyl were studied under the same conditions under which the condensation of these aromatic compounds with methallyl chloride was carried out. However, high yields of the products could not be achieved here. It was of particular interest to carry out the condensation of benzene with 3-chloro-2-chloromethyl-propene-1. But in this case as well, 1,3-dichloro-2-methyl-2-phenylpropane was obtained in yields of only 3–6%. The bulk of the 3-chloro-2-chloromethyl-propene-1 undergoes no changes under the condi-

Table 2

No.	Structural formula	b.p., °C/mm Hg	m.p., °C	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated from bond refr.	Found, % C	Found, % H	Found, % Hal	Calculated, % C	Calculated, % H	Calculated, % Hal
1	$C_6H_5-C(CH_3)_2-CH_2Cl$	76–77/1	–	1.0248	1.5245	52.62	52.77	–	–	37.24	37.33	–	37.4
2	$C_6H_5-C(CH_2Cl)_2-CH_3$	76–77/1	–	1.1603	1.5498	55.06	54.71	–	–	–	–	–	–
3	*p*-$CH_3-C_6H_4-C(CH_3)_2-CH_2Cl$, with admixture of the *m*-isomer	82.5–84/1	–	1.0247	1.5246	54.55	54.64	72.28	8.03	18.92	72.37	8.27	19.40
4	*p*-$C_2H_5-C_6H_4-C(CH_3)_2-CH_2Cl$, with admixture of the *m*-isomer	93–94/1	–	1.0091	1.5216	59.36	59.30	73.51	8.43	18.12	73.26	8.71	18.02

No.	Structural formula	b.p., °C/mm Hg	m.p., °C	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated from bond refr.	Found, % C	Found, % H	Found, % Hal	Calculated, % C	Calculated, % H	Calculated, % Hal
5	*p*-n−C_3H_7−C_6H_4−$C(CH_3)_2CH_2Cl$, with admixture of the *m*-isomer	110—112/3	—	0.9937	1.5156	64.18	63.98	74.33	9.44	16.14	74.52	9.09	16.83
6	*p*-tert-C_4H_9−C_6H_4−$C(CH_3)_2CH_2Cl$	113—114/3	53.5	—	—	—	—	74.95	9.49	15.19	74.80	9.41	15.77
7	Same, with admixture of the *m*-isomer	107—108/1	—	0.9862	1.5146	68.12	68.66	74.75	9.46	15.66	74.80	9.41	15.77
8	*p*-tert-C_4H_9−C_6H_4−$C(CH_3)_2CH_2Br$	137—138/1	36.5	—	—	—	—	62.68	7.95	29.55	62.46	7.86	29.68
9	*p*-C_5H_{11}−C_6H_4−$C(C_3H_7)_2$−CH_2Cl, with admixture of the *m*-isomer	114—116/1	—	0.9780	1.5147	73.57	73.35	75.57	9.56	14.59	75.43	9.79	—

of the reactions. All β-chloro(or bromo)-tert-butylalkylbenzenes readily and in

good yields form organomagnesium compounds, which, in turn, can be successfully used in the Grignard reaction.

Experimental part

Synthesis of the starting halogen derivatives of isobutylene

Methallyl chloride was obtained by chlorination of isobutylene in the gas phase. For the condensation reaction a product was taken with b.p. 70–71°/743 mm, n_D^{20} 1.4280. Literature data ([7]): b.p. 71.5°/760 mm, n_D^{20} 1.4291.

Isocrotyl bromide was obtained in 47–50% yield by dehydrobromination of 1,2-dibromo-2-methylpropane. The dibromide, in turn, was obtained by addition of bromine to isobutylene. Per 1 g-mol of dibromide, 1.2 g-mol of KOH in 180–200 ml of 75–95% ethanol was taken. In all, 900 g of isocrotyl bromide was obtained, with b.p. 91–91.5°, n_D^{20} 1.4610. Literature data ([8]): b.p. 91–91.3°, n_D^{20} 1.4603.

3-Chloro-2-chloromethyl-propene-1 was obtained in 60% yield by chlorination of methallyl chloride in the liquid phase. In all, 850 g of dichloride was obtained with b.p. 133°, n_D^{20} 1.4750. Literature data ([9]): b.p. 53°/45 mm, n_D^{20} 1.4740.

Synthesis of the starting benzene homologs

tert-Butylbenzene was obtained by alkylation of benzene with tert-butyl chloride in the presence of anhydrous ferric chloride ([10]), with b.p. 168–170°, n_D^{20} 1.4920. Yield 80%. Literature data ([11]): b.p. 168.5–170°, n_D^{20} 1.4912.

Neopentylbenzene was obtained from tert-butyl chloride and benzylmagnesium chloride in 63% yield. After distillation over sodium on a column, a fraction was isolated with b.p. 185–187°, n_D^{20} 1.4907. Literature data ([12]): b.p. 185–186°, n_D^{20} 1.4885.

Condensation Reaction

The **condensation reaction** was carried out in a round-bottom flask equipped with a stirrer, dropping funnel, and thermometer. The starting substances were usually taken on the basis of 1 g-mol of the isobutylene halide derivative. Only in the condensation of neopentylbenzene with prenyl chloride and of 3-chloro-2-chloromethylpropene-1 with benzene were the haloalkenyls taken in quantities of 0.5-0.8 g-mol. To a mixture of alkylbenzene with sulfuric acid, with vigorous stirring, the alkenyl halide was added at a rate of 1 g-mol/hour. After the addition was complete, the reaction mixture was stirred for another 12 hours (more prolonged stirring does not affect the yield of the reaction products). The contents of the flask were then washed twice with cold water, with a weak soda solution, and dried over calcium chloride. The alkylbenzene and the starting

haloalkenyl were distilled off at 40–80° and 90–100 mm Hg. The condensation products were isolated by vacuum distillation.

Proof of the structure of β-bromotert-butyl bromide. From the bromide —the product of condensation of benzene with bromoisocrotyl—Grignard reagent was prepared. As a result of the reaction of the latter with carbon dioxide, β-phenylisovaleric acid with m.p. 58–59° was obtained.

$C_{11}H_{14}O_2$.	Found, %:	C 74.32; 74.25; H 7.74; 7.86
	Calculated, %:	C 74.12; H 7.92

Literature data ([3]): m.p. 58–59°.

Oxidation of the condensation products of alkylbenzenes with prenyl chloride. The oxidation was carried out with 20% HNO_3 in an autoclave at 200° for 1.5 hours. For the reaction, 5-gram portions of the haloalkyls were taken, and an amount of 20% HNO_3 1.5 times greater than calculated. The phthalic acids obtained were purified by converting them into ammonium salts. Upon acidification of solutions of ammonium salts evaporated to small volumes, acids were isolated in yields of 66–70%. After 15-hour boiling of 1 g of the acids with 15 ml of methanol and 1.5 ml of conc. H_2SO_4, in all cases dimethyl terephthalate with m.p. 141–142° was obtained in 91–93% yield; it gave no depression of the melting point with an authentic pure sample.

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