ALKYLATION OF BENZENE WITH 4-METHYLCYCLOHEXANOL IN THE PRESENCE OF SULFURIC ACID

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Alkylation of benzene with 4-methylcyclohexanol in the presence of methylcyclohexane and 96, 88, and 80% H_2SO_4 has been studied. It was established that depending on the solubility of the starting components in sulfuric acid, alkylation occurs in the inorganic phase or on the interface between the organic and inorganic phases. The yield and composition of the catalysate are determined to a significant degree by the extent of the alkylation process and intramolecular hydride transfers.

There is disagreement as to which phase (organic, inorganic, interface) supports the alkylation of aromatic hydrocarbons and isoalkanes by alcohols and olefins in the presence of H_2SO_4 [1-4].

In this work alkylation of benzene (B) by 4-methylcyclohexanol (MCHol) in the presence of methylcyclohexane (MCH) and 96, 88, and 80% H_2SO_4 has been studied.

EXPERIMENTAL

Alkylation of benzene with MCHol in the presence of H_2SO_4 and MCH was carried out in the following way. Initially, a mixture of B with solvent and catalyst was stirred for 15 min at 20°C. Then the alcohol was added dropwise and stirred for 30 min at the assigned temperature, after which the upper hydrocarbon layer was separated and the acidic layer was decomposed with water and extracted with ether. The catalysate and ether extracts were combined, washed with water until pH 7, and then dried with $CaCl_2$.

The catalysate composition was determined on a Khrom-4 chromatograph with 360 × 0.3 cm columns, 10% PEG-20,000 on Celite-545, N_2 as carrier gas (80 ml/min), at 160°C for low-boiling and 200° for high-boiling products, programming rate of 3 K/min, using a flame-ionizing detector.

DISCUSSION OF RESULTS

The main experimental data are shown in Table 1. It is evident that upon reaction of B with MCHol in the presence of 96% H_2SO_4 (expt. 1) practically only 1,4-di(1'-methylcyclohexyl)benzene (DMCHB) is formed. Increase of the amount of B (expt. 2) or introduction of 1 mole of MCH (expt. 3) leads to decrease of the product by 30%. It should be expected [5] that the greater the amount of B or solvent used, the higher would be the yield of monocycloalkylbenzenes. However, the obtained data indicate that further increase of MCH (expt. 4), B (expt. 5), or their mixture (expt. 6) leads to increased DMCHB content in the catalysate.

The high yield of disubstituted benzene upon using 96% H_2SO_4 allows one to assume that reaction of B with methylcyclohexyl cations (MCHCs) derived from MCHol occurs in the inorganic phase or in the boundary between the organic and inorganic phases. Formation of DMCHB can be due to the solubility of B and MCH in acid being significantly lower than that of MCHol [6]. As a result [B] in the inorganic phase is low and [MCHC] is high. The latter, reacting with B, forms methylphenylcyclohexanes (MPCH) which are also attacked by MCHCs giving disubstituted benzene.

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TABLE 1. Composition (%) of Catalysates from Sulfuric Acid Catalyzed Alkylation of Benzene by 4-Methylcyclohexanol

Experiment No.	Molar ratio B: MCHol:H_2SO_4:MCH	Alcohol conversion, %	Dimethylcyclohexanes	DMCHB	Methylphenylcyclohexanes	Methylphenylcyclohexanes				Products with bp >300°C
						1,1-	1,2-	1,3-	1,4-	
				96% H_2SO_4						
1	1 : 1 : 10 : 0	100	–	93,1	1,7	100	–	–	–	5,2
2	10 : 1 : 10 : 0	100	–	64,3	30,5	98,0	2,0	–	–	5,2
3	1 : 1 : 10 : 1	100	–	63,9	30,2	97,4	2,6	–	–	5,9
4	1 : 1 : 10 : 10	100	7,8	73,4	13,2	90,2	5,3	1,5	3,0	5,6
5	10 : 1 : 10 : 1	100	0,5	68,3	23,5	94,5	2,6	2,9	–	7,7
6	10 : 1 : 10 : 10	100	–	69,7	24,8	94,8	3,6	1,6	–	5,5
7	10 : 1 : 5 : 1	100	1,1	59,2	36,5	97,8	2,2	–	–	3,7
8	10 : 1 : 2,5 : 1	100	17,9	32,8	44,4	60,8	32,6	4,0	2,0	4,9
				88% H_2SO_4						
9	1 : 1 : 10 : 0	100	5,2	55,4	37,1	92,2	7,3	–	0,5	2,3
10	10 : 1 : 10 : 0	100	7,8	42,1	48,8	88,8	10,1	–	1,1	2,0
11	1 : 1 : 10 : 1	100	6,6	48,0	41,9	84,4	14,8	0,8	–	3,5
12	1 : 1 : 10 : 10	100	26,8	36,2	33,2	58,6	32,0	8,5	0,9	3,8
13	10 : 1 : 10 : 1	100	3,4	44,2	50,8	89,3	9,7	–	1,0	1,6
14	10 : 1 : 10 : 10	100	13,8	45,0	37,9	71,8	22,3	4,2	1,7	3,3
15	10 : 1 : 5 : 1	100	16,0	27,0	56,8	54,3	41,6	–	4,1	0,2
16	10 : 1 : 2,5 : 1	100	35,0	–	65,0	51,1	29,8	5,8	13,3	–
				80% H_2SO_4						
17	1 : 1 : 10 : 0	100	30,3	10,6	56,1	43,7	47,4	5,0	3,9	3,0
18	10 : 1 : 10 : 0	82,2	34,8	–	65,2	38,5	61,5	–	–	–
19	1 : 1 : 10 : 1	100	46,6	2,4	48,6	17,8	79,8	2,4	–	2,4
20	1 : 1 : 10 : 10	79,0	51,0	–	49,0	3,7	88,3	8,0	–	–
21	10 : 1 : 10 : 1	88,9	27,9	–	72,1	36,2	58,9	4,9	–	–
22	10 : 1 : 10 : 10	76,4	35,5	–	64,5	32,6	58,6	5,7	3,1	–
23	10 : 1 : 5 : 1	71,5	24,1	–	75,9	48,1	46,1	5,8	–	–
24	10 : 1 : 2,5 : 1	0	–	–	–	–	–	–	–	–

TABLE 2. Concentration of Sulfuric Acid in the Experiments*

$[H_2SO_4]_0$	Moles of H_2SO_4 in experiment		
	10	5	2.5
96	94,0	92,3	88,8
88	86,2	84,5	79,2
80	78,3	76,7	73,8

*Dilution occurs by water evolved upon dehydration of alcohol.

The ratio of mono- to disubstituted B is affected significantly by the benzene:solvent ratio. Addition of MCH decreases the solubility of B in the inorganic phase, which leads to increased DMCHB yield. It should be noted that in the organic phase, alkylation of MCH by methylcyclohexyl cations occurs with formation of dimethyldicyclohexanes (DMDCHs) (expts. 4 and 5).

Decrease of the H_2SO_4 content from 10 to 2.5 moles (expts. 5, 7, and 8) leads to significant changes in the catalysate composition. DMCHB decreases twofold and the content of MPCH and DMDCH increases correspondingly. Water present in the reaction system (evolved upon alcohol dehydration) changes the H_2SO_4 concentration (Table 2) and its ionic composition [7]. Since the reaction of water with H_2SO_4 proceeds much faster than alkylation [8], the solubility of the organic components, primarily B, in the inorganic phase decreases substantially. Because B dissolves in acid sparingly or not at all, alkylation of B by methylcyclohexyl cations proceeds either in the boundary of the organic and inorganic phases, or in the organic phase. Moreover, in the organic phase DMDCHs accumulate and their formation can proceed by various paths [9, 10].

Upon decrease of the H_2SO_4 content, all MPCH isomers (expt. 8) appear in the catalysate and the amount of 1-methyl-1-phenylcyclohexane decreases by 30% and of the 1,2-isomer increases 12.5 times. This may be because, in the presence of 10 moles of catalyst, secondary MCHCs, which are formed in the inorganic phase from MCHol rearrangement by intramolecular hydride, transfer into thermodynamically more stable tertiary carbocations which react with B to form 1-methyl-1-phenylcyclohexane and with the 1,1-isomer to form DMCHB. For reaction proceeding in the organic—inorganic interface the rate of intramolecular hydride transfer is less, which leads to formation of all MPCH isomers, since isomerization of the 1,1-isomer upon contact with H_2SO_4 does not occur [11].

From the analysis of the results obtained with 96% H_2SO_4 as catalyst (Tables 1 and 2) it follows that decrease of H_2SO_4 concentration should lead to increased yield of monocycloalkylbenzenes and DMDCH and should influence the ratio of MPCH isomers. Experiments with 88 and 80% H_2SO_4 confirmed our assumptions. Upon alkylation in the presence of 88% H_2SO_4 the DMCHB yield decreased by 15.9-37.7% and the content of monocycloalkylbenzenes and DMDCH increased correspondingly. Upon decreasing the catalyst from 10 to 2.5 moles (expts. 13, 15, and 16) these are the only reaction products. The primary catalytic step is a protonation and, according to [12], the activity of solvated protons depends exponentially on the acid concentration; therefore, the rate of these reactions should also depend exponentially on the H_2SO_4 concentration.

Upon using 80% H_2SO_4 the catalysate is composed of monocycloalkylbenzenes and DMDCH. Only in the experiments with low B and MCH content (expts. 17 and 19) were DMCHB and products with bp >300°C found. With change of catalyst amount from 10 to 5 moles, the yield of MPCH isomers increases and the DMDCH yield decreases (expts. 21 and 23). Upon further decrease of the catalyst amount the reaction does not occur. Since B and MCH do not dissolve in 80% H_2SO_4 [6], alkylation of the aromatic hydrocarbon by MCHC proceeds either in the organic—inorganic interface or in the organic phase. Decreased MCHol conversion upon using 80% H_2SO_4 occurs either because MCHol solubility in the inorganic phase decreases or due to a decrease in the rate of the catalytic reactions. This leads to decrease of DMDCH yield upon change of the catalyst amount from 10 to 2.5 moles. The increased amount of 1-methyl-2-phenylcyclohexane is probably due to the rate of intramolecular transfer becoming commensurable with the alkylation rate.

Thus, the experimental results suggest that the yield and composition of the products of benzene alkylation by MCHol depend on a series of competing and mutually connected factors, including solubility of B and MCH in H_2SO_4 and, correspondingly, on whether alkylation proceeds in the inorganic phase or in the boundary between the organic and inorganic phases.

LITERATURE CITED

1. V. G. Lipovich and M. F. Polubentseva, Alkylation of Aromatic Hydrocarbons [in Russian], Khimiya, Moscow (1985), p. 271.
2. A. Z. Dorogochinskii, A. V. Lyumer, and E. G. Vol'pova, Alkylation of Isoparaffins by Olefins with Sulfuric Acid [in Russian], Khimiya, Moscow (1970), p. 216.
3. G. M. Kramer, Alkylation. Investigation and Industrial Implementation of the Process, L. F. Olbrait and A. R. Goldsby (eds.) [Russian translation], Khimiya, Moscow (1982), p. 13.
4. L. F. Olbrait, Alkylation. Investigation and Industrial Implementation of the Process, L. F. Olbrait and A. R. Goldsby (eds.) [Russian translation], Khimiya, Moscow (1982), p. 114.
5. S. D. Mekhtiev, T. A. Pashaev, and F. A. Iseeva, Synthesis and Conversions of Monomeric Compounds [in Russian], Izd. Akad. Nauk AzSSR, Baku (1967), p. 4
6. V. V. Zemskov, Dissertation, Irkutsk (1985).
7. N. G. Zarakhani, V. S. Markin, and G. E. Zaikin, Zh. Phys. Khim., 53, No. 9, 2294 (1979).
8. N. B. Librovich, V. P. Sakun, and N. D. Sokolov, The Hydrogen Bond [in Russian], Nauka, Moscow (1981), p. 174.
9. S. D. Mekhtiev, T. A. Pashaev, and F. A. Iseeva, Synthesis and Conversions of Monomeric Compounds [in Russian], Izd. Akad. Nauk AzSSR, Baku (1967), p. 11.
10. N. K. Deno, Modern Problems of Physical Organic Chemistry [Russian translation], Mir, Moscow (1967), p. 393.
11. N. G. Sidorova, Zh. Obshch. Khim., 32, No. 8, 2642 (1962).
12. L. P. Hammett, Physical Organic Chemistry; Reaction Rates, Equilibria, and Mechanisms, McGraw-Hill, New York (1970).

ANODIC FUNCTIONALIZATION OF OLEFINS IN ALCOHOLS IN THE PRESENCE OF HALIDE SALTS

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Electrolysis of conjugated, unbranched arylolefins in the presence of alkali metal halides in alcohols affords 1-aryl-2-bromoketals in 60-90% yields. Under these conditions, 2-methyl-1-phenylprop-1-ene is converted into 1-bromo-2-methyl-1-phenylprop-1-ene in 80% yield, and arylolefins with no benzylidene hydrogens give 1-aryl-1-alkoxy-2-bromoalkanes.

α-Bromoketones and α-bromoketals are used as intermediates for the synthesis of acyclic and cyclic compounds [1-3]. Specifically, rearrangement of aryl ethyl ketone α-bromoketals affords 2-arylpropionic acids, which possess antiinflammatory activity [4].

α-Bromoketones can be obtained from olefins by oxidation with six equivalents of $NaBrO_2$ in 60-90% yields [5], or by successive or simultaneous treatment with N-bromosuccinimide and the Jones reagent [6, 7] in 70% yield.

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