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## Abstract

## Full Text

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# FREE-RADICAL ADDITION OF ALKYLBENZENES TO $\alpha$-OLEFINS

Hydrocarbon radicals of the aliphatic series readily add to olefins ([1]). The free radicals allyl and benzyl possess extremely low activity in addition and substitution reactions. The low reactivity of these radicals is explained by an inductive displacement of the free electron toward the C=C bond or the aromatic nucleus, i.e., by "delocalization" of the free electron into the general electronic system of the radical as a result of conjugation ([2]). The most characteristic reaction for radicals of this kind is recombination. At the same time, the benzyl radical formed in the decomposition of tert-butyl peroxide in toluene readily adds to anthracene; the cumyl radical under the same conditions does not add to anthracene, but recombines to give 2,3-dimethyl-2,3-diphenylbutane ([3]). There is an indication that ethylene can enter into a telomerization reaction with toluene at a temperature of 260°, pressure of 140 atm, when the process is initiated with cumene hydroperoxide ([4]). However, the composition of the resulting mixture of alkylbenzenes and their structure were not investigated. In the present work we set ourselves the task of studying the possibility of applying the reaction of free-radical addition and telomerization for the synthesis of alkylaromatic hydrocarbons suitable for obtaining surface-active substances of the alkylbenzenesulfonate type. It was established that toluene, ethylbenzene, cumene, *n*-xylene, and $\alpha$-methylnaphthalene are capable of adding to $\alpha$-olefins at a temperature of 150–160° under the action of tert-butyl peroxide. The reaction products are obtained in yields of 10–15%, calculated on the olefin taken. Table 1 gives the quantities of the components and peroxide taken into the reaction, as well as the yields and properties of the addition products. Along with the addition reaction, a substitution reaction of the $\alpha$-hydrogen atom in the olefins by free radicals evidently takes place. The competing substitution reaction may be judged from the bromine numbers determined for some of the products obtained. On the basis of the bromine numbers, the content of unsaturated compounds in the products of addition to olefins is: for toluene, 16–19%; ethylbenzene, 28%; *n*-xylene, 4–6%; $\alpha$-methylnaphthalene, 50%. In all experiments, moreover, crystalline products of dimerization of free radicals were isolated—dibenzyl; 3,4-diphenylbutane; 3,4-dimethyl-3,4-diphenylbutane; di-*n*-xylyl.

Studying the interaction of ethylene with toluene, initiated by tert-butyl peroxide at 200–220° and 140 atm, we established that under these conditions a telomerization reaction takes place, as a result of which monoalkylbenzenes are formed. The first members of the telohomologs formed (propylbenzene, amylbenzene, etc.) may, in turn, serve as telogens, which leads to the formation of secondary and, obviously, tertiary alkylbenzenes. From the reaction mass, five individual hydrocarbons were isolated by distillation (Table 2). The isolation of more highly molecular alkylbenzenes is difficult, since with increasing molecular weight the number of closely boiling isomers and homologs increases. Table 3 gives the fractional composition of the reaction mass after separation from it

**Table 1**

| Experiment no. | Reaction components | Ratios A : B : peroxide, mol | Heating time, h | Addition products | Amount, g-mol | b.p., °C (mm) | $d_4^{20}$ | $n_D^{20}$ | $MR_D$ found | $MR_D$ calc. | $\varepsilon'$ | Number of $CH_2$ groups | Content of tertiary, % | Calculated, % C | Calculated, % H | Found, % C | Found, % H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | A. Toluene B. Undecene-1 | 0.75 : 0.15 : 0.05 | 40 | $C_6H_5C_{12}H_{25}$ | 7 0.03 | 131–135(2) | 0.8570 | 1.4795 | 82.13 | 82.13 | 940 | 11.4 | 15.91 | 87.72 | 12.27 | 87.40 87.50 | 12.37 12.30 |
| 2 | A. Toluene B. Heptene-1 | 1.2 : 0.2 : 0.05 | 36 | $C_6H_5C_8H_{17}$ | 4 0.02 | 132–138(18) | 0.8567 | 1.4865 | 63.61 | 63.63 | 460 | 7.1 | — | 88.16 | 11.84 | 88.38 88.20 | 11.42 11.51 |
| 3 | A. Ethylbenzene B. Hexene-1 | 1.2 : 0.2 : 0.10 | 38 | $C_6H_5CHC_6H_{13}CH_3$ | 4 0.02 | 108–112(15) | 0.8577 | 1.4866 | 68.18 | 63.38 | 300 | 5.5 | — | 88.35 | 11.65 | 88.77 88.35 | 11.57 11.42 |
| 4 | A. Ethylbenzene B. Heptene-1 | 1.2 : 0.2 : 0.11 | 54 | $C_6H_5CH$–$C_7H_{15}CH_3$ | 8.5 0.04 | 120–123(15) | 0.8586 | 1.4856 | 68.21 | 68.38 | 380 | 6.4 | 28.15 | 88.16 | 11.84 | 88.38 88.20 | 11.42 11.51 |
| 5 | A. Cumene B. Octene-1 | 0.48 : 0.12 : 0.06 | 32 | $CH_3C_6H_5$–$C_8H_{17}CH_3$ | 4.5 0.02 | 175–177(6) | 0.8622 | 1.4817 | 77.11 | 77.58 | 380 | 6.4 | — | 87.86 | 12.14 | 87.35 87.41 | 12.17 12.27 |

| Experiment no. | Reaction components | Ratios A : B : peroxide, g-mol | Heating time, h | Addition products | Amount, g-mol | b.p., °C (mm) | $d_4^{20}$ | $n_D^{20}$ | $MR_D$ found | $MR_D$ calc. | $\varepsilon'$ | Number of $CH_2$ groups | Content of tertiary, % | Calculated, % C | Calculated, % H | Found, % C | Found, % H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | A. p-Xylene B. Hexene-1 | 1.1 : 0.2 : 0.13 | 59 | $CH_3C_6H_4C_7H_{15}$ | 0.05 | 129–132(7) | 0.8573 | 1.4887 | 64.03 | 63.63 | 410 | 6.6 | 6.096 | 88.35 | 11.65 | 88.35<br>88.50 | 11.52<br>11.70 |
| 7 | A. p-Xylene B. Nonene-1 | 1.2 : 0.2 : 0.08 | 39 | $CH_3C_6H_4C_{10}H_{21}$ | 0.05 | 139–143(7) | 0.8583 | 1.4870 | 78.05 | 77.58 | 680 | 9.1 | 5.043 | 87.86 | 12.14 | 88.20<br>88.00 | 12.01<br>11.96 |
| 8 | A. α-Methylnaphthalene B. Heptene-1 | 0.9 : 0.2 : 0.06 | 27 | $C_{10}H_9C_8H_{17}$ | 0.04 | 140–146(0.5) | 0.9430 | 1.5547 | 78.93 | 80.74 | 470 | 7.3 | 50.11 | 89.94 | 10.06 | 89.21<br>89.24 | 10.21<br>10.23 |

**Table 2**

| No. | Alkylbenzene | b.p., °C | $d_4^{20}$ | $n_D^{20}$ | $MR_D$, found | $MR_D$, calc. | $\varepsilon'$ | $\varepsilon''$ | Number of groups, $CH_2$ | Number of groups, $CH_3$ | Yield of alkylbenzene* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $C_6H_5-CH_2CH_2CH_3$ | 153–154 | 0,8616 | 1,4906 | 40,38 | 40,40 | 95 | 100 | 2 | 1 | $\frac{51,6}{4,7}$ |
| 2 | $C_6H_5-CH(CH_2CH_3)_2$ | 189–190 | 0,8610 | 1,4873 | 49,55 | 49,69 | 95 | 200 | 2 | 2 | $\frac{23}{2,1}$ |
| 3 | $C_6H_5-CH_2CH_2CH_2CH_2CH_3$ | 196–199 | 0,8576 | 1,4880 | 49,79 | 46,69 | 240 | 100 | 4 | 1 | $\frac{44}{4}$ |

| No. | Alkylbenzene | b.p., °C | $d_4^{20}$ | $n_D^{20}$ | $MR_D$, found | $MR_D$, calc. | $\varepsilon'$ | $\varepsilon''$ | Number of groups, $CH_2$ | Number of groups, $CH_3$ | Yield of alkylbenzene* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | $C_6H_5-CH(CH_2CH_3)-CH_2CH_2CH_3$ | 218—220 | 0,8566 | 1,4845 | 58,96 | 58,99 | 240 | 200 | 4 | 2 | $\frac{36}{3,3}$ |
| 5 | $C_6H_5-(CH_2)_6-CH_3$ | 242—244 | 0,8559 | 1,4851 | 59,06 | 58,99 | 390 | 100 | 6 | 1 | $\frac{108}{9,8}$ |

**Table 3**

| Fraction No. | b.p., °C/mm Hg | Mol. wt. | $d_4^{20}$ | $n_D^{20}$ | $\varepsilon'$ | $\varepsilon''$ | Number of groups, $CH_2$ | Number of groups, $CH_3$ | Fraction yield* |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 100—112/0,5 | 209,4 | 0,8628 | 1,4861 | 300 | 218 | 5 | 2 | $\frac{27}{2,5}$ |
| 2 | 112—126/0,5 | 224,7 | 0,8604 | 1,4845 | 400 | 237 | 6 | 2 | $\frac{57}{5,2}$ |
| 3 | 126—152/0,5 | 248,8 | 0,8612 | 1,4848 | 480 | 250 | 7 | 2,6 | $\frac{64}{5,8}$ |
| 4 | 152/0,5—160/1 | 259 | 0,8606 | 1,4839 | 590 | 238 | 8,5 | 2,4 | $\frac{44}{4}$ |
| 5 | 160—170/1 | 295,8 | 0,8633 | 1,4833 | 690 | 304 | 10 | 3 | $\frac{55}{5}$ |
| 6 | 170/1—180/2 | 321,2 | 0,8597 | 1,4820 | 815 | 325 | 11,5 | 3 | $\frac{26}{2,4}$ |
| 7 | 180—185/2 | 326,3 | 0,8595 | 1,4820 | 785 | 308 | 11 | 3 | $\frac{35}{3,2}$ |
| 8 | 185—190/2 | 336,3 | 0,8588 | 1,4812 | 855 | 314 | 12 | 3 | $\frac{35}{3,2}$ |
| 9 | 190/2—200/1 | 351 | 0,8589 | 1,4812 | 885 | 320 | 12,6 | 3 | $\frac{19}{1,7}$ |

| Fraction No. | b.p., °C/mm Hg | Mol. wt. | $d_4^{20}$ | $n_D^{20}$ | $\varepsilon'$ | $\varepsilon''$ | Number of groups, $CH_2$ | Number of groups, $CH_3$ | Fraction yield* |
|---|---|---|---|---|---|---|---|---|---|
| 10 | 200–210/1 | 392,2 | | 1,4810 | 1000 | 307 | 14 | 3 | $\frac{20}{1,8}$ |
| 11 | 210–240/1 | 434,7 | | | 1215 | 413 | 17 | 4 | $\frac{11}{1}$ |
| Residue | | 876 | | | 2830 | 690 | 38,5 | 7,3 | $\frac{328}{29,8}$ |

* In Tables 2 and 3, the yield above the line is in grams, below the line in percent.

heptylbenzene and lower-boiling products (Table 2). After isolation from the reaction mixture of the individual alkylbenzenes (Table 2) and the higher-boiling fractions listed in Table 3, a solid product (residue) resembling paraffin, with m.p. 45–46° and average molecular weight 876, was obtained. IR spectra were obtained for the products of free-radical addition and for the telomerization products. From the intensity of the bands at $2930 \pm 5$ cm$^{-1}$ ($\varepsilon'$) and $2960 \pm 5$ cm$^{-1}$ ($\varepsilon''$), corresponding to the valence asymmetric vibrations in the $CH_2$ and $CH_3$ groups, the number of these groups in the samples studied was determined. A directly proportional relationship is observed between $\varepsilon''$ and the number of $CH_3$ groups; between $\varepsilon'$ and the number of $CH_2$ groups a directly proportional relationship is observed at $n \geq 3$. Tables 1, 2, and 3 give the values of $\varepsilon'$ and $\varepsilon''$ and the corresponding numbers of

$CH_2$ and $CH_3$ groups for each sample studied. The average error of the measurements was ~3%. The determinations were carried out by E. D. Lubuzh.

## Experimental Part

**Addition of alkylbenzenes to $\alpha$-olefins.** All addition reactions were carried out in a steel autoclave of 200 ml capacity at 150–160°. The peroxide was added in portions of 2–2.5 g at approximately equal time intervals to the cooled autoclave. We give a description of one of the experiments (experiment No. 6, Table 1). A mixture consisting of 115 g (1.1 g-mol) of *p*-xylene, 18 g (0.2 g-mol) of 1-hexene, and 3 g of peroxide was heated in an autoclave for 6 h. The remaining 16 g of peroxide was added in 2-g portions after 5–8 h intervals. Distillation of the reaction mixture gave 10 g (0.05 g-mol) of *p*-methylheptylbenzene and 14 g (0.07 g-mol) of di-*p*-xylene with m.p. (after recrystallization from alcohol) 82–82.5°. The content of unsaturated compounds in *p*-methylheptylbenzene, calculated from bromine numbers, was 6.09; 5.05%; calculated from iodine numbers, 4; 4.5%.

**Telomerization of ethylene with toluene.** The reactions were carried out in a steel two-liter autoclave equipped with a stirrer, at 200–220° and an ethylene pressure of 130-140 atm. Into the ice-cooled autoclave were charged 640 g (6.25 g-mol) of toluene, and ethylene was introduced under a pressure of 40 atm. The autoclave was heated to 220°, the pressure rising to 140 atm. After this, with stirring, a solution of 9 g (0.06 g-mol) of tert-butyl peroxide in 40 ml of toluene was introduced into the reaction mass. Heating of the autoclave was continued for another 10 h, after which toluene was distilled off from the reaction mass. An 89 g amount of higher-boiling residue was obtained. Increasing the amount of peroxide introduced increases the amount of telomerization products formed. Thus, when 10, 20, and 30 g of peroxide were used (introduced in 5-g portions), 110, 163, and 200 g, respectively, of high-boiling products were obtained. The high-boiling substances obtained in nine experiments (1100 g) were first separated by simple distillation into three broad fractions: A—with b.p. up to 260°—286 g (26%), B—with b.p. 260° (760 mm)—290° (2 mm), 542 g (49.3%), and C—residue (solid), 268 g (24.4%). Fraction A was distilled over metallic sodium, giving 273 g of a colorless transparent liquid, which was fractionated on a column. Distillation on the column gave five individual alkylbenzenes, whose purification from impurities was carried out by chromatography on a column packed with silica gel. Table 2 gives the structures and properties of these hydrocarbons. Their amounts are given without allowance for intermediate fractions, the weight of which was 82.7 g. The amount of heptylbenzene is the sum from fraction A (27 g) and from fraction B (81 g). Fraction B was separated by distillation over sodium into narrower fractions, the properties, molecular weight, and amounts of which are given in Table 3. The high-molecular telomerization products (fraction C and 60 g of residue obtained in the distillation of fraction B) had m.p. 44–45°, molecular weight 876. According to elemental analysis, the carbon content in them is 86–43%, hydrogen 13.58%. The ultraviolet spectrum indicates the presence of aromatic rings in these products.

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

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