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Abstract

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Chemistry

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ON THE ISOTOPIC EXCHANGE OF HYDROGEN IN HEXASUBSTITUTED BENZENES

Hydrogen atoms of aliphatic C—H bonds in molecules of alkylbenzenes do not enter into the reaction of isotopic hydrogen exchange in acidic media even under very severe conditions (in anhydrous DF in the presence of BF_3) ([1], [2]). In accordance with this, we found that both hexamethylbenzene (I) and hexaethylbenzene (II) practically do not enter into the reaction of isotopic hydrogen exchange with deuterosulfuric acid.

However, hexasubstituted benzene derivatives containing, as substituents, three cycloalkane rings fused with the benzene ring are capable of entering into the reaction of isotopic hydrogen exchange with acids. We found that the hydrocarbons tricyclotetramethylbenzene (III) and tricyclotrimethylbenzene (IV) enter into the reaction of isotopic exchange both with deuterosulfuric acid and with deuterium chloride (in the latter case in the presence of anhydrous $FeCl_3$). The results of experiments on isotopic exchange with D_2SO_4 in nitrobenzene medium are given in Table 1.

(III) (IV)

Table 1

Substance	Hydrocarbon	D_2SO_4	$C_6H_5NO_2$	Duration of exchange, h	Temp., °C	Experiment	Calculation for β-hydrogens
I	1	6.2	62.2	25	25.0	45	40 880(α)
II	1	5.2	75.9	24	25—25	190	24 360
II	1	4.8	72.5	24	50.0	60	23 370
II	1	8.2	73.8	6	70.0	110	31 820
III	1	8.4	71.5	49	20—25	26 500	29 100
III	1	7.4	93.1	23	25.0	14 600	27 540
III	1	7.4	80.9	48	25.0	24 200	27 600
III	1	7.4	80.9	123	25.0	30 500	27 600
III	1	7.4	80.9	241	25.0	30 400	27 600

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Substance	Hydrocarbon	D_2SO_4	$C_6H_5NO_2$	Duration of exchange, h	Temp., °C	Experiment	Calculation for β-hydrogens
III	1	7.4	80.9	24	30.2	20 700	27 600
III	1	7.4	80.9	48	30.2	28 300	27 600
III	1	8.4	80.9	123	30.2	27 400	27 600
IV	1	6.9	50.4	24	20—25	3470	23 200
IV	1	7.7	47.4	49	20—25	8100	23 800
IV	1	7.4	77.9	21	25.0	7300	23 670
IV	1	7.4	77.9	72	25.0	21 000	23 670
IV	1	7.4	77.9	96	25.0	22 600	23 670

Having compared the proton resonance (p.r.) spectra of the initial hydrocarbons and of those isolated after exchange, we established that the exchange reaction proceeds in the β-position. In molecules III and IV there are two types of hydrogen atoms: α- and β-atoms with respect to the benzene ring. The p.r. spectrum of III consists of two peaks of equal intensity with shifts $\tau_\alpha = 7.4$ and $\tau_\beta = 8.2$ (Fig. 1*a*). The assignment of the peaks in the p.r. spectrum of III was made on the assumption that the inductive effect of the benzene ring should lead to different shielding of the α- and β-protons by the electrons of the C—H bonds. Compared with the α-protons, the β-protons are shielded to a lesser extent; therefore the β-proton signal is located in the stronger field, and the α-proton signal in the weaker field. An additional check of this assignment was also made from the p.r. spectrum of IV, where the signals from the α- and β-protons are unambiguously determined by their different integral intensities and by spin-spin interaction. At a frequency of 40 MHz the spin-spin splitting was poorly resolved, but the spectrum at 60 MHz (Fig. 1*b*) clearly demonstrated the presence of a triplet signal in the weak field ($\tau_\alpha = 7.4$) and a quintuplet signal of half the integral intensity in the strong field ($\tau_\beta = 8.05$), which completely confirms the assignment made earlier.* In the p.r. spectra of the hydrocarbons isolated after exchange, the signal of the β-protons decreases, whereas the signal

Fig. 1. P.r. spectra of initial III (*a*), initial IV (*b*)

Fig. 2. P.r. spectra of III isolated after exchange (*a*) (deuterium content 30.4 at.%), and of IV (*b*) (deuterium content 21.0 at.%)

of the α-protons remains unchanged (Fig. 2). Measurement of the ratio of inte-

···of the integral intensities of the signals in the NMR spectra shows good agreement with the ratio calculated theoretically from the isotope-analysis data (Table 2).

Table 2

Hydrocarbon	Excess density of the combustion water of the sample, γ/ml	Ratio of integral intensities of the α- and β-proton peaks: experiment	Ratio of integral intensities of the α- and β-proton peaks: calculated for exchange of only β-atoms
III	23 500	2.00 : 1.19	2.00 : 1.06
III	30 400	2.00 : 0.84	2.00 : 0.78
IV	8100	2.00 : 0.67	2.00 : 0.76
IV	21 000	2.00 : 0.40	2.00 : 0.37

To determine the relative reactivity of III and IV, the kinetics of the isotopic exchange of hydrogen was studied. As is seen from the data in Table 1, equilibrium of the exchange reaction for III is reached at 30.2° in 48 h. For IV the exchange proceeds at a lower rate. The first-order rate constants of isotopic exchange, calculated from the equation, are given in Table 3.

Table 3

Kinetics of isotopic exchange of III (at the ratio hydrocarbon : D_2SO_4 : $C_2H_5NO_2 = 1 : 7.4 : 93.1$ and temperature 25°)

Average	5	7	9	13	17	23
Duration of exchange, h						

* We express our gratitude to P. V. Petrovskii and V. I. Sheichenko for the p.r. spectra.

	Average	5	7	9	13	17	23
Excess density of combustion water, γ/ml	–	4450	5850	7400	10 250	12 600	14 600
$K_{io} \cdot 10^6$ s^{-1}	9.7	9.8	9.6	9.6	9.9	10.0	9.1

Table 4

Kinetics of isotopic exchange of IV (at the ratio hydrocarbon : D_2SO_4 : $C_6H_5NO_2 = 1 : 7.4 : 78.8$ and temperature 25°)

	Average	15.5	21.5	27.5	42.75
Duration of exchange, h					
Excess density of combustion water, γ/ml	–	5935	7275	8650	13 200
$K_{io} \cdot 10^6$ s^{-1}	5.0	5.1	4.7	4.6	5.3

The data obtained make it possible to put forward an assumption concerning the mechanism of the reactions found. Apparently, the reaction begins with oxidation of the α-carbon atom of the side ring by deuterosulfuric acid, with formation of carbonium ions (V and VI), which are in equilibrium with the corresponding olefins:

(V): carbonium-ion structural formula $\rightleftharpoons$ corresponding olefin structural formula

(VI): carbonium-ion structural formula $\rightleftharpoons$ corresponding olefin structural formula

Further isotopic exchange occurs through reversible addition and elimination of a proton (deuteron). The proton (deuteron) is directed to the β-position, since the carbonium center in the α-position is stabilized more strongly through conjugation with the benzene ring than is the carbonium center in the β-position. Work to elucidate the mechanism of the reactions found will be continued by us.

Experimental Part

Tricyclotetramethylbenzene (dodecahydrotriphenylene, III) was obtained by the method of S. V. Svetozarskii (^{3}) and purified by repeated recrystallization from benzene, sublimation, and zone melting. For the experiments a preparation with m.p. 232–233°, whose UV spectrum coincides with the literature data, was used.

Tricyclotromethylbenzene (trindane, IV) was obtained by the method of R. Mayer (^{4}) and purified by recrystallization from methanol and by zone melting. For the experiments a gas-chromatographically pure preparation with m.p. 96–97° was used.

Hexamethylbenzene (I) was obtained by passing a mixture of phenol and methanol vapors, with a large excess of the latter (molar ratio 1 : 15), over alumina at 380–410° (^{5}). For the experiments a gas-chromatographically pure preparation, purified by recrystallization from absolute ethanol and by zone melting, m.p. 164–165°, was used.

Hexaethylbenzene (II) was obtained by ethylation of benzene with ethyl chloride by the Friedel–Crafts method (^{6}). The preparation was purified by recrystallization from absolute ethanol. The gas-chromatographically pure preparation had m.p. 129–130°.

Experimental procedure. A weighed portion of substance (0.5–0.9 g) is dissolved in 30–35 ml of nitrobenzene purified and distilled on a column; the required amount of 100% D_2SO_4 is added, the mixture is stirred, and it is placed in a thermostat. In the case of III and IV, the color of the nitrobenzene solution changes to dark red; in the case of I and II, no change in coloration is observed. To quench the reaction, the reaction mixture is poured into 100 ml of a 10% $NaHCO_3$ solution. The nitrobenzene layer is washed repeatedly with water and dried over $MgSO_4$. The nitrobenzene is distilled off under vacuum in a nitrogen atmosphere; the remaining hydrocarbon is sublimed or recrystallized. In experiments with IV, the residue after removal of nitrobenzene is chromatographed on an Al_2O_3 column, using *n*-hexane as eluent. With this treatment it is possible to isolate 50–70% of the initial charge taken into the reaction.

The NMR spectra were recorded on a YaMR-TsLA-5535 spectrometer; verification of spin-spin splitting in IV was carried out on an INM-C-60 spectrometer. CCl_4 was used as solvent, and tetramethylsilane (TMS) as internal standard.

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