Chemistry

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Abstract

Full Text

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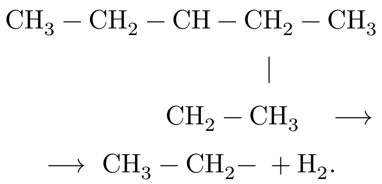
Cyclization of 3-Ethylpentane to Ethylcyclopentane

Recently we have published several papers in which it was reported that paraffin hydrocarbons can undergo cyclization in the presence of platinum with formation of a five-membered ring. At first this was shown [1,2] by means of Raman spectra using the examples of *n*-heptane, *n*-octane, and isooctane (2,2,4-trimethylpentane). Subsequently the cyclization of isooctane was studied in greater detail [3]: a sufficiently large amount of hydrocarbon was brought into contact with the catalyst in order to carry out precise fractionation on an efficient column. As a result of the fractionation, the cyclization product of isooctane –1,1,3-trimethylcyclopentane–was isolated in individual form. In this way the possibility of the direct formation of cyclopentanes from paraffins was demonstrated quite reliably.

It seemed important to us, for comparison, to investigate some other hydrocarbon, one not so highly branched as isooctane. At the same time, of course, it was desirable that this hydrocarbon, like isooctane, should give only one cyclization product, boiling sufficiently far from the starting hydrocarbon. This would again make it possible to isolate the cyclization product in individual form.

Fig. 1. Fractionation curve of the catalyzate

As such an object, 3-ethylpentane was chosen, which has only one side chain and is capable, upon cyclization, of giving a single reaction product–ethylcyclopentane:



$$\begin{array}{c} CH_3-CH_2-\underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}}-CH_2-CH_3 \quad \longrightarrow \\ \longrightarrow\ CH_3-CH_2- \ +H_2. \end{array}$$

The difference between the boiling temperatures of these two hydrocarbons is 10°, and therefore their separation on an efficient column is not very difficult.

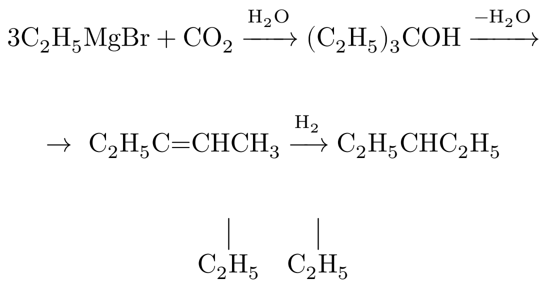
The starting hydrocarbon was passed over the catalyst once at 310° and a space velocity of 0.19-0.22 h^{-1}. Five portions of hydrocarbon, totaling 215.7 g, were passed over one catalyst sample, and the catalyzates from each portion were collected separately. In view of the limited amount of hydrocarbon at our disposal, the last two portions consisted of unreacted 2-ethylpentane isolated from the first three catalyzates by distillation on a column.

Analysis of the catalyzates showed that they contained 1.2-1.9% olefins and 0.4-0.7% aromatic hydrocarbons. After removal of these reaction products by chromatography, the content of ethylcyclopentane in the catalyzates could be determined from the constants (12.5-5.7%), decreasing from run to run.

By distillation of the combined dearomatized catalyzate it was possible to isolate individual ethylcyclopentane, as is evident from the distillation curve shown in Fig. 1. The constants of fraction V of this distillation practically do not differ from the constants of ethylcyclopentane.

Experimental part

3-Ethylpentane was obtained from ethylmagnesium bromide and carbon dioxide via triethylcarbinol and 3-ethylpent-2-ene by the method previously developed by us (4):



$$3C_2H_5MgBr + CO_2 \xrightarrow{H_2O} (C_2H_5)_3COH \xrightarrow{-H_2O}$$

$$\to C_2H_5\underset{\substack{|\\ C_2H_5}}{C}{=}CHCH_3 \xrightarrow{H_2} C_2H_5\underset{\substack{|\\ C_2H_5}}{CH}C_2H_5$$

After careful purification by distillation on a column of 100 theoretical plates and by chromatography on silica gel, the 3-ethylpentane had the following constants: b.p. 93.4°/760 mm, n_D^{20} 1.3934, d_4^{20} 0.6982, which practically does not differ from the constants of this hydrocarbon according to the most reliable literature data (5): b.p. 93.475°/760 mm, n_D^{20} 1.39339, d_4^{20} 0.69816.

As catalyst, as in the preceding works, platinized charcoal (20% Pt), prepared according to Zelinsky, was used. This catalyst preparation at 300° and a space velocity of 0.9-1.0 converted cyclohexane into benzene to the extent of 87-92%.

Over 50 ml of such catalyst at 310° and a feed space velocity of 0.19-0.22 hr^{-1}, three portions of 3-ethylpentane were passed over the course of three days. In all, 129.9 g of hydrocarbon were passed through, and three catalyzates were collected, the yields and properties of which are given in Table 1 (experiments 1–3). After determination of the constants and bromine numbers, the catalyzates were chromatographed on silica gel to separate olefins and aromatics. The properties of the catalyzates after chromatography are also given in Table 1. The content of unsaturates was found from the bromine number; the content of aromatics, from the difference between the refractive indices of the catalyzate before and after chromatography (with correction for unsaturates), which, for such low concentrations of these hydrocarbons, is apparently the most accurate method. The yield of cyclopentanes was also determined refractometrically on the basis of the additivity of the refractive indices of paraffinic and naphthenic hydrocarbons in binary mixtures.

Table 1

Yield and properties of the products of cyclization of 3-ethylpentane

Experiment No.	3-Ethylpentane passed through, g	Catalyst and its properties: weight, g	Catalyst and its properties: n_D^{20}	Catalyst and its properties: d_4^{20}	Catalyst and its properties: unsaturated, %	Catalyst and its properties: aromatic, %	Properties of catalyzates after chromatography: n_D^{20}	Properties of catalyzates after chromatography: d_4^{20}	Properties of catalyzates after chromatography: aniline point, °C	Ethylcyclopentane content, %
1	34.7	31.7	1.3973	0.7077	1.2	0.7	1.3967	0.7066	62.6	12.5
2	34.7	32.1	1.3971	0.7070	1.7	0.7	1.3964	0.7057	63.0	11.4
3	50.5	–	1.3960	0.7041	1.9	0.4	1.3956	0.7042	63.8	8.3
4	59.0	56.4	1.3958	–	–	–	1.3950	0.7024	–	6.1
5	36.8	35.1	1.3954	–	–	–	1.3949	–	–	5.7

The combined chromatographed catalyzate (89.4 g) was subjected to distillation on a column of 100 theoretical plates. After a small fore-cut fraction (b.p. 80.7 –93.2°/760 mm, n_D^{20} 1.3925, d_4^{20} 0.6977, anilinoling point 64.4°, weight 5.6 g) 86 ml (59 g) of substance with n_D^{20} 1.3932 was collected. This fraction was passed over the same catalyst (see Table 1, experiment 4), and, after chromatography and determination of the constants, the catalyst was added to the residue from the preceding distillation on the column. The newly distilled fraction of 3-ethylpentane, weighing 36.8 g, was again passed under the previous conditions over the same catalyst (see Table 1, experiment

5) and, after chromatography and determination of the constants, was added to the residue from the preceding distillation. The concentrate thus obtained, weighing 63.3 g, was carefully distilled on the same column. The results of this distillation are given in Fig. 1 and in Table 2.

Table 2

Results of distillation of the catalyzate

Fraction No.	Boiling limits in °C at 760 mm	Fraction yield, g	Fraction yield, %	n_D^{20}	d_4^{20}	Content of cyclopentane hydrocarbons, %, per fraction	Content of cyclopentane hydrocarbons, %, per [[unclear: dehydrogenized]] catalyzate
I	90.6—93.3	4.2	6.5	1.3925	0.6977	10—15	0.6—0.9
II	93.3—93.5	24.1	37.3	1.3934	—	—	—
III	93.5—94.1	17.5	27.1	1.3934	—	—	—
IV	94.1—103.35	6.2	9.5	1.4055	0.7299	51	4.7
V	103.35—103.5	4.9	7.5	1.4196	0.7657	99	7.4
Residue	—	7.7	11.9	1.4195	—	99	11.8
Total		6.46					

As can be seen from Table 2, fraction V has constants very close to the most reliable data for ethylcyclopentane (5): b.p. 103.466°/760 mm; n_D^{20} 1.41951, d_4^{20} 0.76647.

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