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Abstract

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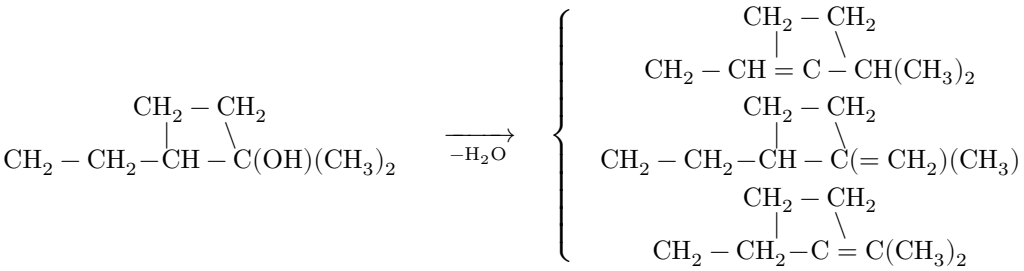
DEHYDRATION OF DIMETHYLCYCLOPENTYLCARBINOL IN THE PRESENCE OF SULFURIC ACID

In 1955 we showed ([1]) that, when dimethylcyclobutylcarbinol is distilled with 0.1% (based on the weight of the carbinol) of concentrated sulfuric acid, it undergoes dehydration, forming a mixture of the two possible cyclobutane hydrocarbons with a double bond in the side chain: isopropenyl- and isopropylidenecyclobutanes. Both hydrocarbons were isolated from the mixture by distillation on an efficient rectifying column and characterized by means of physicochemical constants and spectra of combinational light scattering.

In the present work we applied this method of dehydration to another tertiary alcohol—dimethylcyclopentylcarbinol—with the aim of determining how a five-membered ring would influence the course of the reaction. Carrying out the dehydration of dimethylcyclopentylcarbinol under the same conditions as before, i.e., with 0.1% conc. H_2SO_4, we likewise obtained a mixture of unsaturated hydrocarbons. By distillation on a 100-theoretical-plate column, three individual hydrocarbons were isolated: isopropylcyclopentene-1, isopropenylcyclopentane (obtained for the first time), and isopropylidenecyclopentane. Consequently, the dehydration proceeded according to the scheme:



The structure of the isolated hydrocarbons was confirmed by the agreement of the constants of two of them with literature data, as well as by an investigation of the combinational scattering spectra of all three.

It is evident from the experimental part that in the combinational scattering spectrum* of isopropylidenecyclopentane there are almost all the lines previously noted as characteristic in frequency and intensity for alkylidenecyclopentanes (using ethylidene-, propylidene-, and butylidenecyclopentanes as examples) ([3]), i.e., 905(76), 1025(28), 1214(15), 1229(17), 1432(54), and 1685(140). In the spectrum of isopropylidenecyclopentane there is no line in the region 425–435 cm^{-1} ([3]); it is apparently due to vibrations of the side chain and,

* The method for measuring the spectra was described earlier ([2]).

naturally responds to changes in its structure. It is not excluded that in the spectrum of isopropylidenecyclopentane it corresponds to the line 353 (43).

The spectra of isopropenylcyclopentane and isopropylcyclopentene-1 show considerable similarity to one another and differ substantially from the spectrum of isopropylidenecyclopentane: as a rule, the lines are less intense and broader, and a considerable background is observed throughout the spectrum in both cases. In the spectrum of isopropylcyclopentene-1 all the lines are present that were previously noted as characteristic of 1-alkylcyclopentenes (using ethyl-, propyl-, and butylcyclopentenes-1 as examples) ([3]): 891(29), 908(20), 1017(19), 1034(15), 1206(14), 1645(84), 3056(70). It is also very characteristic of spectra of hydrocarbons of this type that, of the two lines in the region 1440–1460 cm^{-1}, the first is considerably more intense than the second. Instead of one intense line in the region 1025 cm^{-1}, the spectrum of isopropylcyclopentene-1 shows two: 1017 and 1034 cm^{-1}. The frequency of the double-bond line is somewhat lowered: 1645 instead of 1659 cm^{-1} ([3]). The spectrum of isopropenylcyclopentane has all the characteristic features due to the presence in the molecule of a five-membered ring and a double bond in the side chain; the frequency of the latter is also somewhat below the usual values: 1646 instead of 1650–1652 cm^{-1}.

The present work had already been begun when the article by Kurloglu and Van Valle ([4]) appeared, devoted to the study of the dehydration of dimethylcycloalkylcarbinols having three-, four-, five-, and six-membered rings. Dehydration of the carbinols was carried out by distilling them with 0.01% conc. H_2SO_4. In the authors' opinion, in the case of carbinols with three-, four-, and five-membered rings, only hydrocarbons with an isopropenyl group were formed. Only in the case of dimethylcyclohexylcarbinol did the authors detect in the dehydration product, along with isopropenylcyclohexane, small amounts of isopropylidenecyclohexane (7%) and isopropylcyclohexene (2%). In connection with work ([4]), we also studied the dehydration of dimethylcyclopentylcarbinol with 0.01% conc. H_2SO_4; the reaction was carried out under the same conditions as before.

Having at our disposal the combination-scattering spectra of all possible dehydration products, we used them to investigate the composition of the hydrocarbons obtained with 0.01% H_2SO_4. Taking into account the closeness of the spectra of isopropenylcyclopentane and isopropylcyclopentene-1, we used for analysis the spectral region with $\Delta\nu$ 300–400 cm^{-1}, where isopropenylcyclopen-

tane has a line 374(23), and isopropylcyclopentene-1 a line 322(23). The latter, however, is overlapped by the line 322(13) of isopropylcyclopentane, which makes the analysis difficult and lowers the accuracy of its results because of inevitable errors in allowing for the overlap. In addition, the accuracy of the analytical results is reduced by a rather strong background in this region of the spectrum; therefore we used the following procedure. From the line 1685 cm^{-1}, the content of isopropylidenecyclopentane was determined accurately by direct comparison with its standard sample. The contents of isopropenylcyclopentane and isopropylcyclopentene-1 were estimated from the intensity of the lines in the region 300-400 cm^{-1} and additionally checked against the lines in the region 1000-1050 cm^{-1}.

The data obtained from analysis, using the combination-scattering spectra, of the mixture of unsaturated hydrocarbons obtained in the dehydration of dimethylcyclopentylcarbinol with 0.1% H_2SO_4 are in agreement with the distillation curve of this mixture on a rectification column. The product obtained with 0.01% conc. H_2SO_4 is likewise a mixture of three hydrocarbons: isopropylcyclopentene-1, isopropenyl- and isopropylidenecyclopentane; however, the ratio of these components in the mixture changes with the amount of H_2SO_4 taken for dehydration. As it is increased, the content of isopropenylcyclopentane falls from (68-63% to 40-35%), while isopropylidenecyclopentane and isopropylcyclopentene-1 increase. The yield of dehydration products also increases (from 66 to 91%). Thus, the results we obtained do not agree with the data reported in the article

^(4). It should be noted that the substances to which Kourdoglou and Van Walle ascribe the structures of isopropenylcyclobutane and isopropenylcyclopentane differ greatly in constants from the corresponding hydrocarbons isolated by us in a sufficiently pure form, and apparently are not individual hydrocarbons but mixtures of unsaturated hydrocarbons with different positions of the double bond.

Experimental Part

Dimethylcyclopentylcarbinol was synthesized by the action of methylmagnesium bromide on the ethyl ester of cyclopentanecarboxylic acid. B.p. 68-70°/12 mm, n_D^{20} 1.4590; d_4^{20} 0.9138; yield 78% of theory, calculated on the ester of cyclopentanecarboxylic acid taken into the reaction. In all, 300 g of dimethylcyclopentylcarbinol was synthesized.

Dehydration of dimethylcyclopentylcarbinol with 0.1% conc. H_2SO_4. 84 g of dimethylcyclopentylcarbinol was heated with 85 mg of acid in a flask connected to a rectification column with glass packing. As dehydration of the carbinol proceeded, the hydrocarbons distilled off and were collected together with the water in a receiver. The hydrocarbon layer was washed with water, with a solution of $NaHCO_3$, again with water, dried over fused $CaCl_2$, and distilled from a Favorsky flask at 120-139°. 66 g (91%) of dehydration product

Fig. 1. Distillation curve of the product of dehydration of dimethylcyclopentylcarbinol in the presence of 0.1% conc. H_2SO_4

Figure 1: Fig. 1. Distillation curve of the product of dehydration of dimethylcyclopentylcarbinol in the presence of 0.1% conc. H_2SO_4

was obtained, n_D^{20} 1.4512; d_4^{20} 0.8107. In all, from two experiments 115.5 g of dehydration product was obtained. Raman spectrum of the dehydration product: $\Delta\nu$ (in cm^{-1}): 214(0), 272(0), 292(0), 320(1), 352(2), 372(2), 396(0), 418(1), 449(0), 481(3), 527(3), 538(1), 579(2), 608(1), 625(1), 676(0), 710(4), 743(0), 788(0), 805(1), 832(2), 844(2), 889(6), 902(7), 954(3), 1002(2), 1026(3), 1067(2), 1101(3), 1117(1), 1140(2), 1166(1), 1189(2), 1211(0), 1227(2), 1256(1), 1274(2), 1294(3), 1346(0), 1378(5), 1393(0), 1438(7), 1451(7), 1468(1), 1486(0), 1506(1), 1549(1), 1567(0), 1588(2), 1624(1), 1646(10), 1684(10).

Fig. 1. Distillation curve of the product of dehydration of dimethylcyclopentylcarbinol in the presence of 0.1% conc. H_2SO_4

The resulting mixture of hydrocarbons (87 g) was fractionated on a column with copper packing, efficiency 100 theoretical plates. The results of the fractionation are given in Fig. 1.

Fraction 123.1-123.3° (760 mm) is isopropenylcyclopentene-1; n_D^{20} 1.4436; d_4^{20} 0.8007; MR_D 36.53, calculated for C_8H_{14} with one double bond 36.48 (lit.^(5): b.p. 123.0-123.2°; n_D^{20} 1.4443; d_4^{20} 0.7988). Raman spectrum of isopropenylcyclopentene-1: $\Delta\nu$ (in cm^{-1}): 223(3), 247(2), 293(2), 322(23), 358(9), 377(0), 400(1), 411(1), 444(10), 473(5), 502(3, b, f), 527(1), 582(4), 607(3), 650(2, b), 761(1, f), 784(3, b), 814(7, b, f), 841(29), 891(29), 908(20), 920(7), 947(13), 959(17), 1017(19), 1034(15), 1069(12), 1099(13), 1117(8), 1135(5), 1149(2), 1177(8), 1206(14), 1239(2), 1251(8), 1277(1), 1296(26), 1306(17), 1441(64), 1464(35), 1495(2, b), 1525(2), 1565(1), 1645(84, b), 2843(220), 2867(190), 2899(250), 2912(240), 2936(100, f), 2968(200), 3056(70).

Fraction 128.9° (760 mm) is isopropenylcyclopentane; n_D^{20} 1.4479; d_4^{20} 0.8072; MR_D 36.54. Raman spectrum of isopropenylcyclopentane: $\Delta\nu$ (cm^{-1}): 208(10, b), 322(13, b), 365(10, f).

374 (23), 435 (2), 467 (8, w), 498 (6, w), 525 (5, ph), 541 (15), 592 (1, w), 653 (2, w), 704 (10, dbl?), 732 (3, w), 791 (4, w), 832 (9), 851 (10, w), 889 (50), 945 (7), 991 (3, w, ph), 1003 (23), 1035 (15, dbl), 1067 (7), 1090 (7), 1155 (10), 1182 (2, w, ph), 1208 (2, w, ph), 1241 (4, w, ph), 1271 (2, ph), 1289 (13), 1305 (8), 1335 (5), 1371 (4), 1393 (18), 1434 (25, ph), 1448 (39), 1478 (8, ph), 1502 (3, ph), 1646 (96, w), 2850 (70, ph), 2869 (150), 2892 (50, ph), 2913 (190), 2947 (210), 2964 (200), 2987 (100), 3012 (20, ph), 3079 (70, dbl?).

The fraction 139.0° (760 mm) is isopropylidenecyclopentane; n_D^{20} 1.4587; d_4^{20} 0.8182; MR_D 36.80 (lit.^(5): b.p. 137-138°; n_D^{20} 1.4597; d_4^{20} 0.8202).

Raman spectrum of isopropylidenecyclopentane: $\Delta\nu$ (in cm^{-1}): 223(3,ph),

353(43,w), 486(38), 524(23), 545(1), 575(12), 596(3), 620(4), 712(34), 743(2), 770(4, w), 826(19), 847(7), 905(76, r), 927(2), 960(11), 1012(6), 1025(28), 1067(10), 1100(9, w), 1168(11), 1190(1), 1214(15), 1229(17), 1255(3), 1274(12), 1297(8), 1316(3), 1333(2), 1370(10, ph), 1378(41), 1432(54), 1451(66), 1471(24), 1490(0), 1539(4, w), 1604(1), 1658(3), 1685(140, w), 2834(150), 2860(270), 2885(240), 2909(330), 2936(250), 2955(240), 2979(120, ph).

The composition of the dehydration product is given in Table 1.

Dehydration of dimethylcyclopentylcarbinol with 0.01% conc. H_2SO_4. Under the same conditions as in the experiments with 0.1%, 70 g of dimethylcyclopentylcarbinol was dehydrated with 7 mg of conc. H_2SO_4. The dehydration product obtained had b.p. 120–139°, 40 g (66.6%), n_D^{20} 1.4505; d_4^{20} 0.8122.

Table 1

Hydrocarbon	By distillation curve, %	By spectra, %
Isopropylcyclopentene-1	~25	25–30
Isopropenylcyclopentane	~40	40–35
Isopropylidenecyclopentane	~35	35

Raman spectrum of the dehydration product: $\Delta\nu$ (in cm^{-1}): 213(1), 232(0), 252(0), 271(1), 292(0), 319(2), 353(2), 373(3), 398(0), 420(1), 437(1), 487(2), 527(3), 539(4), 577(1), 613(0), 640(0), 655(0), 676(0), 698(0), 710(5), 743(0), 767(0), 787(0), 803(0), 826(2), 841(1), 853(2), 888(6), 902(6), 941(1), 957(1), 1004(3), 1025(2), 1041(2), 1066(3), 1084(1), 1099(2), 1148(2), 1162(2), 1189(2), 1216(2), 1230(2), 1263(0), 1293(3), 1332(1), 1376(4), 1388(3), 1436(3), 1447(8), 1472(2), 1518(1), 1544(2), 1583(2), 1645(10), 1685(9).

The composition of the dehydration product on the basis of Raman spectra: 10–15% isopropylcyclopentene-1, 68–63% isopropenylcyclopentane, 22% isopropylidenecyclopentane.

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