[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

Spectrographic Study of the Formation of 1,3-Cyclohexadiene from Cyclohexene

BY HILDEGARD STÜCKLEN, HELEN THAYER AND PHYLLIDA WILLIS

In the preparation of highly purified cyclohexene for absorption spectrum measurements in the Schumann region the preliminary examination with the quartz spectrograph indicated the presence of traces of both benzene and 1,3-cyclohexadiene, although the values for refractive index, density, and boiling point ($n^{20}{}_D$ 1.4460, $d^{20}{}_4$ 0.8101, b. p. 82.7°) were in good agreement with those reported by recent investigators. The preparation has been studied in detail not only to obtain the material free from these impurities but also to trace their formation.

The absorption spectrum of cyclohexene shows a broad step-out of low intensity between 34,000 and 44,000 cm.$^{-1}$,[1] whereas that of 1,3-cyclohexadiene in this region is characterized by a very intense absorption band which has three distinct maxima at the top of the band.[2] The three sharp bands reported by Mohler and Lohr[3] in the absorption spectrum of cyclohexene undoubtedly are due to traces of the diene since as little as 10^{-5} mole per liter can be detected readily spectrographically. Although the well-known and very characteristic absorption bands of benzene in this region are much less intense than those of the diene, their maximum extinction coefficient is still one thousand times that of cyclohexene and hence spectrographic measurements may be used for the detection of minute amounts of either benzene or 1,3-cyclohexadiene.

Earlier experiments had shown that both benzene and cyclohexadiene were present after the first distillation of the cyclohexene and must have been formed in the reaction mixture; the benzene could be removed by careful fractionation but continued fractionation seemed to increase the amount of diene. The present study has shown that it is possible to remove the diene by treatment with maleic anhydride and to obtain pure cyclohexene if the excess maleic anhydride is removed by low temperature filtration. When this material was distilled at atmospheric pressure, or when exposed to light, the diene, but not the benzene, reappeared; evidently both heat and light are influencing factors in the reaction. The results suggest, also, that traces of peroxide in the cyclohexene may be a factor.

Experimental

Spectrographic Measurements.—Extinction coefficients using a hydrogen lamp as light source were determined for the liquid cyclohexene by the method previously described.[4] Where measurements were made in the spectral region below 2400 Å., a copper–silver spark was used and the extinction coefficients for the hexane solution were determined by the well-known Henri method. Figure 1 gives the absorption spectrum curve for pure cyclohexene and its hexane solution, concn. 0.894 to 0.081 *M*. Since a continuous background is necessary for the detection of the diene, the curves in Fig. 2 are based on measurements of the liquid cyclohexene with the hydrogen lamp as light source.

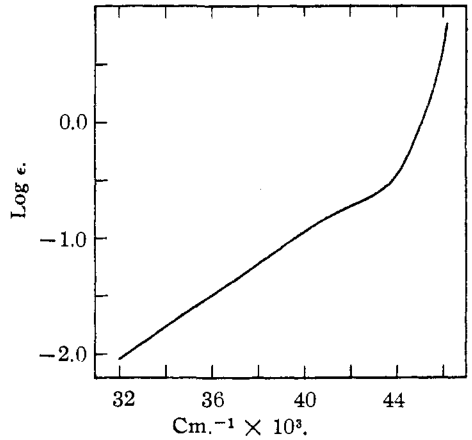

Fig. 1.—Absorption spectrum curve of cyclohexene.

Cyclohexene was prepared by the dehydration of cyclohexanol (Eastman Kodak Co., m. p. 22°). Comparative study of the product obtained from cyclohexanol which had been purified by vacuum distillation with that from undistilled material showed no detectable difference in purity so that most of the preparations were made from the cyclohexanol without further purification. When anhydrous oxalic acid was used as dehydrating agent (200 g. of oxalic acid to 40 g. of cyclohexanol) the absorption spectrum of[5] the product (79% yield) indicated the presence of 1,3-cyclohexadiene and also a benzene derivative, although benzene itself was not identified. This latter impurity was removed by careful fractionation just as benzene was but the oxalic dehydration offered no advantage over sulfuric acid treat-

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[1] Hartley and Dobbie, *J. Chem. Soc.*, **77**, 848 (1900); Stark and Levy, *Jahrb. Radioakt. Elektronik*, **10**, 179 (1913); Arnold and Kistiakowsky, THIS JOURNAL, **54**, 1720 (1932); Alsopp, *Proc. Roy. Soc.* (London), **A143**, 618 (1933); **146**, 302 (1934).

[2] V. Henri and L. W. Pickett, *J. Chem. Phys.*, **7**, 439 (1939).

[3] Mohler and Lohr, *Helv. Chim. Acta*, **20**, 1183 (1937).

[4] H. Stücklen, *J. Opt. Soc.*, **29**, 37 (1939).

[5] Zelinsky and Zelikow, *Ber.*, **34**, 3252 (1901); Alsopp, *Proc. Roy. Soc.* (London), **A143**, 618 (1933).

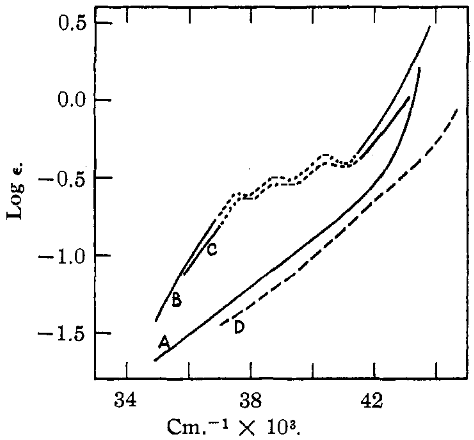

Fig. 2.—A, Purified cyclohexene (Sample I); B, cyclohexene (Sample II), after one month; C, cyclohexene (Sample III), after one month; D, cyclohexene (Samples II, III, and IV), after three months.

ment[6] which was used for a number of preparations. Special precautions were taken to exclude oxygen during the preparation and purification process. The reaction flasks and distilling columns were heated and cooled in a stream of dry nitrogen and the nitrogen-filled apparatus was protected from the oxygen of the air through pyrogallol absorption. Nitrogen was bubbled through all solutions used in washing the cyclohexene. In each preparation the crude product was collected in two approximately equal portions, the first distillate (Fraction A) b. p. 71 to 73°, the remainder of the material (Fraction B) b. p. 73 to 90°. Each of these fractions was washed with sodium hydroxide and water until neutral, dried over lime, and distilled separately through Fenske columns (150 × 2 cm., packed with 1-turn 4-mm. glass helices) of the total reflux partial take-off type. Samples of each of these fractions were examined spectrographically before fractionation; the higher concentration of benzene was shown in fraction A, while fraction B gave no spectral evidence of benzene but showed a considerable amount of diene. This does not necessarily mean the complete absence of benzene in this fraction since a study of hexane solutions containing different proportions of benzene and cyclohexadiene had shown that benzene in the presence of diene cannot be detected by absorption spectrum measurements where the proportion of diene to benzene is as great as two to one. In the distillation of A approximately one-third of the material was collected before complete removal of the benzene, while with B about one-sixth of the total was sufficient to remove all of the benzene and once removed there was no evidence of its reappearance. It was not possible to remove the diene by the most careful fractionation.

Removal of 1,3-cyclohexadiene from the benzene-free fractions of the cyclohexene was accomplished by treatment with maleic anhydride (m. p. 55°, 1 g. to 25 g. of cyclohexene). The mixture was refluxed for several hours and then distilled through a Fenske column (35 × 1.5 cm.); in every case crystals (m. p. 138–145°) appeared in the top of the column. When this material was recrystallized from petroleum ether, the m. p. (145°) showed it to be 3,6-endoethylene-Δ^4-tetrahydro-*o*-phthalic anhydride (m. p. 147°).[7] The absorption spectrum of the distillate showed the removal of the diene but indicated the presence of an impurity which shifted the absorption toward longer wave lengths. This proved to be maleic anhydride which was dissolved in the cyclohexene. It was crystallized out when the cyclohexene was cooled to −78°. Redistillation of the cyclohexene diminished the amount of maleic anhydride present but brought about the reappearance of the 1,3-cyclohexadiene, thus showing the impossibility of preparing diene-free cyclohexene by methods which involved heating the material. The most satisfactory purification is summarized as follows. After removal of benzene by fractionation, the benzene-free distillate is refluxed with maleic anhydride for two to three hours, cooled and the addition product and the excess maleic anhydride removed by filtration; the filtrate is then washed with water, dilute sodium hydroxide, and again with water and dried over lime. The cyclohexene is cooled to −78° (dry-ice and alcohol) and filtered; one repetition of this process is ordinarily sufficient to remove the last traces of maleic anhydride. Purification by low temperature vacuum distillation was tried but proved to be no more satisfactory than the low temperature filtration. Absorption measurements of this cyclohexene showed it to be entirely free from benzene, diene, and maleic anhydride; n^{20}_{D} 1.4460, d^{20}_{4} 0.8104.

The effect of ultraviolet light on cyclohexene in the absence and in the presence of traces of peroxide and of aldehyde was investigated by irradiating the material with the light of the hydrogen lamp. Baly absorption tubes of quartz were used for this irradiation to avoid transfer of the material for the absorption spectra measurements and three samples of cyclohexene, purified as described, were examined. Care was taken to exclude air from the tubes and the spectrum was photographed through a fixed length for all exposures. Since cyclohexene, like all unsaturated hydrocarbons, oxidizes readily, the different samples always were tested for the presence of aldehyde and peroxide; the freshly prepared material was free from both but traces of peroxide developed within a few days and on longer standing the aldehyde was present but no considerable amount of peroxide was ever observed. For exposure to ultraviolet light one sample of cyclohexene, free from peroxide and aldehyde, one containing a trace of aldehyde but no peroxide, and one containing a trace of both aldehyde and peroxide were used. Each of these samples was irradiated for three hours and measurements of their absorption spectra were made at intervals of twenty to thirty minutes. Although completely free from diene at the beginning, the spec-

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(6) "Organic Syntheses," Vol. V, 1925; Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 141 (1936).

(7) Diels and Alder, *Ann.*, **460**, 115 (1928).

trum showed that each sample developed diene within twenty minutes; the aldehyde-peroxide free material (sample I) showed the smallest amount, that containing aldehyde (sample II) the next and the sample (III) containing both aldehyde and peroxide the largest amount. This same relationship was shown on longer irradiation; sample I, after irradiation for three hours, indicated a diene concentration approximately the same as sample II after one hundred and forty minutes and sample III after one hundred and twenty minutes. The refractive indices increased from 1.4460 to 1.4463 during irradiation.

The effect of sunlight on cyclohexene in the presence and absence of air was determined. Four 30-g. samples of purified material, $n^{20}\mathrm{D}$ 1.4460, containing a slight trace of peroxide, were treated as follows. Two were placed in Pyrex glass tubes which had previously been evacuated and then filled with nitrogen and the tubes were sealed at diminished pressure (samples I and II); the other samples (III and IV) were sealed in Pyrex tubes containing air. Sample I, the control, was left in the dark at a temperature of about +10°, the others were placed on the roof. At the end of a month (March with fourteen days of sunshine) samples II and III were opened; both samples showed the same increase in refractive index, $n^{20}\mathrm{D}$ 1.4464, and a small amount of diene, as shown by their absorption spectra (Fig. 2) had developed in each sample. The material was re-sealed as before and placed on the roof for an additional two months when the contents of the four tubes were examined. The control (sample I) showed no change in refractive index nor in absorption spectrum except for a decrease in intensity below 42,000 cm.$^{-1}$; samples II and III ($n^{20}\mathrm{D}$ 1.4464) which had given definite evidence of diene after one month now had no diene present; sample IV which had not been opened was practically identical with II and III and all the samples except the control had minute droplets of a gummy substance on the walls of the tube. This gum was insoluble in all ordinary solvents and is probably a polymerization product but it was not investigated further. All of the samples which had been exposed to light gave a slight test for the presence of aldehyde but were peroxide free and in each case the material had developed a pleasant orange-like odor, quite different from the pure hydrocarbon and similar to that observed in the residue from the first distillation of the cyclohexene. The data are insufficient for generalization but it is of importance to note that while the emission spectrum of the sun ends at 3100 Å., in a region where the extinction coefficient of cyclohexene is extremely low (about 0.01), yet cyclohexadiene developed and later disappeared through polymerization. The fact that the original material contained a trace of peroxide, while none of the samples except the control showed any peroxide after three months suggests the possibility that the presence of peroxide may be an influencing factor in this reaction.[8]

Summary

1. Through ultraviolet absorption spectra measurements the presence of minute amounts of 1,3-cyclohexadiene and benzene have been detected in all samples of cyclohexene prepared by dehydration of cyclohexanol, although the amounts are too small to have measurable effect on other physical constants.

2. Benzene was removed completely by careful fractionation of the cyclohexene and did not reappear during the course of the investigation (six months).

3. Long-continued distillation of cyclohexene increased the diene content; this could only be removed by treatment with maleic anhydride. In the subsequent distillation of the diene-free cyclohexene, 1,3-cyclohexadiene reappeared.

4. A method of purification which involves low temperature filtration was worked out and the ultraviolet absorption spectrum of pure cyclohexene was measured.

5. The formation of diene by the action of (1) ultraviolet light and (2) sunlight, on cyclohexene has been studied. In the latter case, the diene disappeared after long standing, possibly through polymerization. The effect of air and of peroxide as influencing factors in the photochemical reaction was considered.

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(8) The preparation and purification of the materials used in this study have been carried out under the direction of Professor Mary L. Sherrill, of this Laboratory, to whom the writers are greatly indebted for her careful guidance and active interest.