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ISOLATION AND PROPERTIES OF 1,1,2,3,3a,7a-HEXACHLORO-3a,4,7,7a-TETRAHYDRO-4,7-METHANOINDENE

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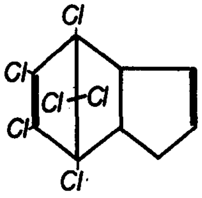
DURING the IR spectroscopic investigation of chromatographic fractions of heptachlor, which contained unreacted chlordene /4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene/ /I/, an unknown compound /II/ was discovered between chlordene and heptachlor with characteristic absorption bands at 691, 744, 1173 and 1211 cm^{-1}. These bands were also present in the IR spectra of /I/, which was prepared by Diels-Alder reaction of hexachlorocyclopentadiene /III/ with cyclopentadiene /IV/ in molar ratio 1 : 1 at temperatures between 85 and 100°C. Samples of /I/, prepared under these conditions, contained 15-20% of /II/, determined by IR analysis.

It was found, that pure /I/ can be prepared from such products by simple crystallization from methanol. The purity of /I/ was verified by repeated chromatography and IR spectra. Concentrates, containing about 70% of /II/ can be obtained from methanolic mother liquors by recrystallization and pure /II/ can be isolated from these by means of column chromatography. A silicagel /containing 4% w/w of water/ - petroleum ether /b.p. 40-60°C/ column was used. Fractions, containing more than 98%

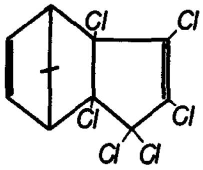
of /II/ were rechromatographed, fractions with identical IR spectra were combined and recrystallized from pentane, resulting in a few grams of white crystalline substance /II/, which did not contain detectable amounts of /I/.

M.p. 155°C, is not characteristic. Found: C, 35.56; H, 1,69; Cl, 62.79. Calc. for $C_{10}H_6Cl_6$: C, 35.44; H, 1.79; Cl, 62.77%. Infrared spectra of /I/ and /II/ are in Fig. 1. The positions of absorption bands of /II/ are /in cm^{-1}/: 568, 599, 658, 691, 718, 744, 796, 809, 876, 891, 902, 921, 936, 955, 968, 985, 1005, 1045, 1071, 1132, 1173, 1211, 1252, 1330, 1388, 1463, 1632, 2891, 2963, 3000.

The result of analysis indicates, that /II/ is an isomer of /I/ and that therefore, considering the mode of preparation, the structural formula /V/ or /VI/ may be assigned to /II/.



/V/ exo? - /I/



/VI/

Preparation of /I/ according to Riemschneider[1,2] was reproduced and the resulting products were analysed by IR spectrophotometry.

At molar ratio /III/:/IV/ = 1 : 1 and maximum reaction

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[1] R. Riemschneider, Monatsh. 83, 810 /1952/.

[2] R. Riemschneider, Oester. Apotheker Zt. 6, 250 /1952/.

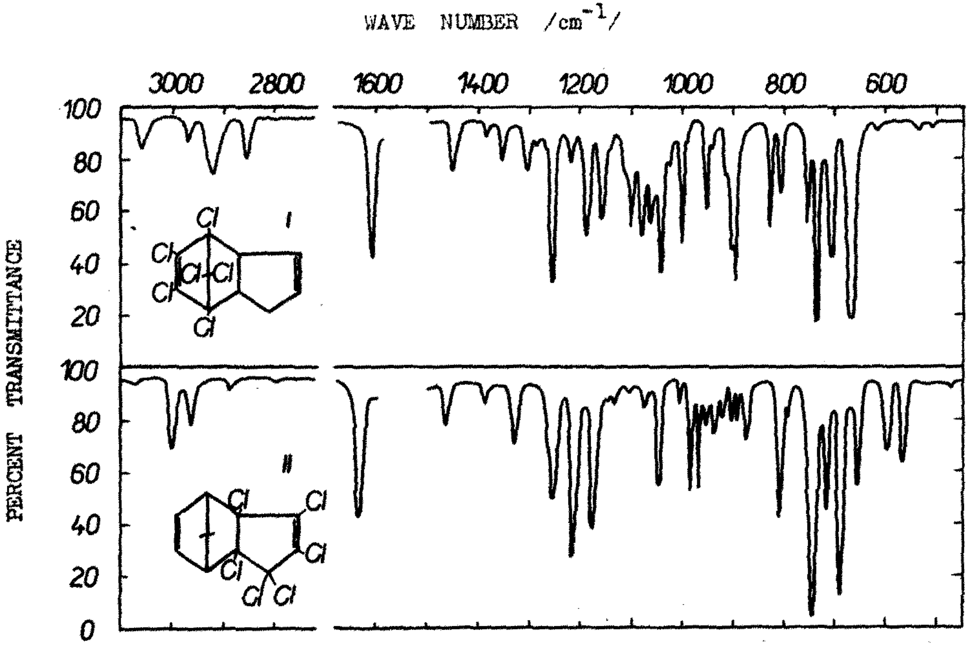

FIG. 1. Infrared spectra of 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene /I/ and 1,1,2,3,3a,7a-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene /II/ in carbon disulfide, 36.5 mg/ml, 0.28 mm cell.

temperature 145°C a yield /crystallized /I// 60% of theoretical value had been reported [1]. In this experiment it was found, that the composition of the reaction product depends on maximum reaction temperature. The following compositions were determined /in w/w per cent/: /I/ 83.5, 91.9; /II/ 10.3, 1.2; /III/ 1.6, 1.1; /IV/ 0.4, 0.3; dicyclopentadiene /VII/ 1.7, 1.3 at 105°C and 177°C respectively.

At molar ratio /III/:/IV/ = 1 : 1.5 and maximum reaction temperature 117°C a yield /crystallized /I// 94% of theoretical value had been reported [1]. According to Riemschneider [1] the reaction mixture had been heated to 160°C at the end of the reaction time to detect the presence of unreacted /III/, this is not reported in the publication [2], although the yield is reported the same. In this experiment it was found, that at 107°C /after removing unreacted /IV/ under vacuum/ the reaction product contained /in w/w per cent/: /I/ 76.9; /II/ 18.4; /IV/ 0.3; /VII/ 2.6. After heating for one hour at 160°C this composition changed to: /I/ 93.9; /II/ 1.0; /VII/ 1.5.

The results of these experiments indicate, that

a/ isomerization of /II/ to /I/ occurs readily at temperatures above 160°C,

b/ the maximum temperature of the reaction mixture and not molar ratio of reagents is the governing factor in the preparation of pure /I/.

Thermal isomerization of /II/ to /I/ was studied in solid state at temperatures between 115 and 145°C and the following values of the first-order k constant /in sec^{-1}/ were found: 1.04×10^{-4} at 115°C; 4.97×10^{-4} at 130°C and 1.88×10^{-3} at 145°C. The temperature dependence $\log k = 13.6 - 6.82/T$

results in an activation energy value of 31.2 kcal/mole. This is close to 34 kcal/mole for the monomerization of dicyclopentadiene and therefore too high for an endo-exo isomerization. This observation is in agreement with great differencies between IR spectra of /II/ and /I/.

Whether the chlorine atoms in compound /II/ are attached to the [2.2.1] bicycloheptene or the cyclopentene ring was proved by following reactions:

a/ determination of chlorine hydrolysable with silver nitrate in glacial acetic acid [3], specific for chlorine atoms in position 1 . It was found that /II/ had two hydrolysable chlorine atoms, while /I/ did not react with the reagent.

b/ addition of phenylazide [4] to the unsubstituted double bond of the [2.2.1] bicycloheptene ring [5]. Compound /II/ reacted quantitatively with phenylazide, while /I/ did not react.

On basis of these results the unknown compound /II/ can be stated to be 1,1,2,3,3a,7a-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene /VI/. Structure /VI/ is in agreement with frequency shifts of the olefinic C-H and C=C stretching vibrations in the spectra of /II/ and /I/.

Surprising is the fact, that the compound /II/ is a product of Diels-Alder reaction of hexachlorocyclopentadiene with cyclopentadiene, in which hexachlorocyclopentadiene acts as a dienophile, which is in contradiction with conclusions of

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[3] M. Kleiman, Brit. pat. 698,213, Oct. 7, 1953.

[4] H. Ritter and F. Gude, Brennstoff Chem. **38**, 173 /1957/.

[5] P.J. Wilson Jr. and J.H. Wells, Chem. Rev. **34**, 16 /1944/.

Riemschneider and Grabitz [6], who studied the reaction of hexachlorocyclopentadiene with a series of cyclic dienes and stated, that hexachlorocyclopentadiene reacts exclusively as a diene. Thermal isomerization of 1,1,2,3,3a,7a-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene to 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene is a new example of rearrangement described by Woodward and Katz [7] for 1-hydroxydicyclopentadiene /to 8-hydroxydicyclopentadiene/ and by Yates and Eaton[8] for 4,5,6,7-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-8-one /to 2,3,3a,7a-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1-one/.

The chlorination of the compound /II/ to an isomeric heptachlor will be reported later.

We thank J. Drábek, C.Sc., V. Bátora, C.Sc. and J. Macko for helpful discussions and interest in this work.

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[6] R. Riemschneider and B.E. Grabitz, Monatsh. **91**, 26 /1960/.

[7] R.B. Woodward and T.J. Katz, Tetrahedron **5**, 70 /1959/.

[8] P. Yates and P. Eaton, ibid. **12**, 13 /1961/.