Tetrahedron Letters No. 1, pp. 21-26, 1961. Pergamon Press Ltd. Printed in United States of America

# A DIMER OF CYCLOBUTADIENE

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(Received 13 December 1960)

IN this communication a preliminary report is presented concerning a dimer of cyclobutadiene, formed in the decomposition of the previously described $C_4H_4 \cdot AgNO_3$ complex. [1]

As it was shown, [1] on treatment of this complex with water, a volatile compound is evolved with the elementary composition $C_1H_1$. If the decomposition of the silver nitrate complex is carried out with an aqueous solution of sodium chloride in the presence of an organic solvent, solutions of the decomposition product are obtained. The gas-chromatogram of the ethereal solution thus prepared reveals the presence of only one component, in the range corresponding to a $C_8$ hydrocarbon.

A solution in ethyl chloride obtained as indicated above, leaves after evaporation of the solvent a colourless liquid which was analysed mass-spectrometrically. The

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[1] M. Avram, E. Marica and C. D. Nenitzescu, Chem.Ber. 92, 1088 (1959).

mass-spectrogram thus obtained is identical with the mass-spectrogram of the volatile compound evolved in the thermal dissociation of the complex $C_4H_4 \cdot AgNO_3$ heated under vacuum. Ionizing tensions of 2o and 4o volts were employed. A principal peak of mass number (MN) 1o4 is observed, together with a smaller peak of MN 1o3 and an isotopic peak of MN 1o5. Besides these, the only other important peaks have MN 52 and 51, accompanied by smaller peaks with MN 53 and 5o. At ionizing tensions of 4o volts or more, the intensities of peaks 51 and 52 are about the same as of peak 1o4, while at 2o volts ionizing tension, peak 52 is about 1oo times smaller than peak 1o4. The conclusion emerges that the compound obtained from the $C_4H_4 \cdot AgNO_3$ complex is a $C_8H_8$ hydrocarbon which under electron impact undergoes, besides the usual hydrogen splittings, a breakdown into $C_4H_4$ molecules, and that this breakdown is definitely favoured over other possible breaking modes.

The infrared absorption spectrum of the $C_8H_8$ compound was then determined in $CS_2$ (66o-133o $cm^{-1}$) and $CCl_4$ solution (133o-181o ; 226o-33oo $cm^{-1}$). A table of band maxima is appended. The IR spectrum was also determined of the $C_8H_8$ in gaseous state, by decomposition of the $C_4H_4 \cdot AgNO_3$ complex with a sodium chloride solution in heavy water, in an evacuated cell. The vapour spectrum differs from the solution spectrum through small shifts due to the change

Infra-red frequencies of $C_8H_8$ in solution
($CS_2$ 660-1330 $cm^{-1}$ ; $CCl_4$ 1330-3300 $cm^{-1}$)

| | | |
|---|---|---|
| 3094 | (M) | C - H stretching |
| 3033 | (S) | |
| 2975 | (VS) | |
| 2967 | (VS) | |
| 1710 | (VW) | |
| 1700 | (VW) | |
| 1640 | (W) | |
| (1550) | (W) | C = C stretching (in gas only) |
| 1305 | (W) | |
| 1288 | (S) | C - H deformation |
| 1208 | (W) | |
| 1190 | (W) | |
| 1164 | (M) | C - C stretching |
| 1152 | (M) | |
| 1050 | (W) | |
| 990 | (W) | |
| 966 | | |
| 957 | (M) | $C_4$ ring deformation |
| 915 | | |
| 912 | (W) | |
| 890 | (W) | |
| 880 | (W) | |
| 820 | (M) | C - H deformation |
| 810 | (M) | |
| 792 | (S) | |
| 775 | (W) | |
| 745 | (M) | |
| 732 | (M) | |

(W) weak, (M) medium, (S) strong and (VS) very strong bands. The relative intensities only were estimated.

in aggregation state (ca. 10 $cm^{-1}$), through the appearance of a weak band at 1550 $cm^{-1}$ which cannot be seen in the solution spectrum (in this region $CCl_4$ presents itself absorption), through fine structure of the 800 $cm^{-1}$ band in the vapour spectrum (780-830 $cm^{-1}$), and through the splitting in two of the 735 $cm^{-1}$ band in the solution spectrum.

The IR spectrum is relatively simple and agrees with a provisionally proposed structure of a tricyclooctadiene (I) for the $C_8H_8$ compound. Unsaturated character is manifested in the presence of CH stretching bands at 3094 and 3033 $cm^{-1}$. The double band at 2967-2975 $cm^{-1}$ is probably due to CH stretching of the saturated central ring in (I), with a displacement towards higher frequencies owing to ring strain. A band, similar in position (2970 $cm^{-1}$) and intensity was found also in the tricyclic dimer of benzocyclobutadiene [2] (II). In the low frequency region there appear deformation vibrations of saturated and olefinic C-H bonds. The intense band at 1288 $cm^{-1}$ can be assigned to the deformation vibration of the C-H bond in the saturated ring, and the band at 957 $cm^{-1}$ is probably due to the deformation vibration of the four-membered saturated rings. The 1550 $cm^{-1}$ band in the vapour spectrum is undoubtedly a C=C stretching vibration of double bonds in the side-rings. A band at 1566 $cm^{-1}$ has been found in the cyclobutene spectrum. [3]

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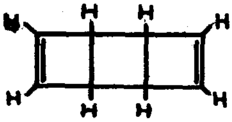
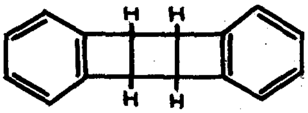
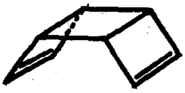
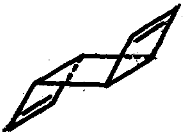
[2] M. Avram, D. Dinu and C.D. Nenitzescu, Chemistry and Industry 1959, 257.

[3] R. C. Lord and D. G. Rea, J.Amer.Chem.Soc. 79, 2401 (1957).


(I)


(II)


(III)


(IV)

The proposed structure (I) involves a dimerization of cyclobutadiene through cycloaddition, similarly with the dimerizations observed with benzocyclobutadiene, [2] tetramethylcyclobutadiene, [4] and 1,3-diphenylcyclobutadiene. [5]

From the two possible configurations (III) and (IV), the <u>trans</u>-structure (IV) with $C_{2h}$ symmetry is more probable on symmetry grounds.

The ethereal solution of the $C_8H_8$ dimer yields on treatment with silver nitrate solution a $C_4H_4 \cdot AgNO_3$ complex, identical in every respect, IR spectrum included, with the initial $C_4H_4 \cdot AgNO_3$ complex. In a detailed analysis of the IR spectrum of this silver nitrate complex, Fritz, McOmie and Sheppard have shown [6] that the spectrum provides support for a monomeric formulation $C_4H_4 \cdot Ag\ NO_3$,

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[4] R. Criegee and G. Louis, Chem. Ber. **90**, 417 (1957)
R. Criegee, G. Schröder, G. Maier and H. G. Fischer, Chem. Ber. **93**, 1553 (1960).

[5] E. H. White and H. C. Dunathan, Amer.chem.Soc. Meeting Chicago, Sept. 1958, Abstracts p. 41 P ; cited after E. Vogel, Angew. Chem. **72**, 4 (1960).

[6] H. P. Fritz, J. F. W. McOmie and N. Sheppard, Tetrahedron Letters **1960**, under print.

involving $C_4H_4$ units as hydrocarbon ligands. This means that when the silver-nitrate complex is formed from the dimer, a dissociation $C_8H_8 \longrightarrow 2\ C_4H_4$ must take place. Although inusual, such a hypothesis would not be altogether excluded because breakage of single bonds on complexation of olefinic ligands with metals was observed in some cases.[7, 8] Also, considerable stabilization for cyclobutadiene on complexation with metals may be anticipated. Attempts to solve this problem chemically, with larger amounts of substance, are under way.

The mass-spectrometric determinations were performed by Professor N. Martalogu and Miss D. Mumuianu from the Institute of Atomic Physics, Bucharest, to whom our best thanks are given. We also are particularly grateful to Dr. J. F. W. McOmie, Dr. N. Sheppard and Dr. H. Fritz for discussions.

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[7] R. B. King and F. G. A. Stone, J.Amer.chem.Soc. 82, 4557 (1960).

[8] B. F. Hallam and L. P. Pauson, J. 1958, 646.