Tetrahedron Letters No.26, pp. 2137-2139, 1969. Pergamon Press. Printed in Great Britain.

STRUCTURES OF THE DIMERS OF PERCHLOROBUTENYNE.

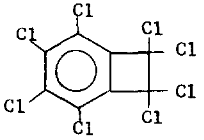
OCTACHLOROCYCLOOCTATETRAENE AND OCTACHLOROBICYCLO-[4.2.0]-OCTATRIENE-[2.4.7]

Alfred Roedig and Rudolf Helm
Institut für Organische Chemie der Universität Würzburg

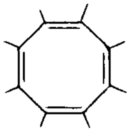
Robert West and R. Martin Smith
Department of Chemistry, University of Wisconsin, Madison, Wisconsin, USA

(Received in USA 7 April 1969; received in UK for publication 1 May 1969)

Perchlorobutenyne[1] undergoes dimerization at 80-100° into α-C_8Cl_8, m.p. 103°, which at higher temperature (160-180°) or in the presence of aluminum chloride is rapidly transformed into β-C_8Cl_8, previously identified as perchlorobenzocyclobutene, I.[1] Treatment of α-C_8Cl_8 with protonic acid catalysts induces transformation to a third isomer, γ-C_8Cl_8, m.p. 172°.[2] The latter compound is remarkably inert to electrophilic reagents and oxidizing agents. For example, it is inert to bromine, aqueous potassium permanganate, and ozone, and even survives boiling with fuming nitric acid. On the basis of its infrared, ultraviolet and especially the nuclear quadrupole resonance (nqr) spectrum, we now identify γ-C_8Cl_8 as octachlorocyclooctatetraene, II.



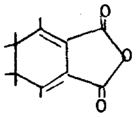
I



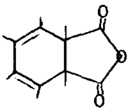
II

Compound II shows nqr lines[3] all falling within a narrow region, at the following frequencies in MHz (relative intensities in parentheses): 36.60 (2), 37.13 (4) and 37.27 (2). This spectrum suggests that all 8 chlorine atoms have nearly identical chemical environment; the frequencies are normal for vinyl chlorines.[4] The extremely simple infrared spectrum (only four bands at 1570, 1160, 900 and 730 cm^{-1}) and zero dipole moment for the compound demand a structure of high symmetry. In the ultraviolet, γ-C_8Cl_8 shows a maximum at 237 nm ($\log \epsilon = 4.47$) and a shoulder at 275 nm but no absorption above 300 nm. The uv spectrum, and the infrared absorption at 1570, rule out the alternative octachlorocubane structure. The remarkable inertness of II must result from steric shielding of the double bonds by the bulky chlorine atoms. Similar extreme unreactivity due to steric shielding has been found for octakis(trifluoromethyl)cyclooctatetraene.[5]

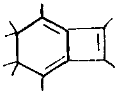
The bis(methylene)bicyclohexene structure previously proposed for α-C_8Cl_8 on the basis of its Raman spectrum[6] seems inconsistent with the results of ozonization experiments. In ethyl acetate at -45°, α-C_8Cl_8 is converted by ozone into a thermolabile compound $C_8Cl_6O_3$, which upon refluxing in ether eliminates chlorine and is converted to tetrachlorophthalic acid anhydride. The ozonization product must therefore have structure III or IV, suggesting either V or VI as structures for α-C_8Cl_8.



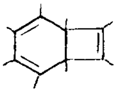
III



IV



V



VI

Ultraviolet or infrared spectra do not allow a decision to be made between structures V and VI, but the nqr spectrum strongly suggests that VI is correct. α-C_8Cl_8 has nqr lines at 35.53 (1), 35.95 (1), 36.99 (2), 37.91 (1), 38.18 (1), 39.63 (1), 39.91 (1). The lines at 35.5-36.0 MHz, an unusually low frequency, suggest vinyl chlorines in a cyclobutene ring (cf. hexachlorocyclobutene, vinyl chlorine resonance at 35.65 and 35.78).[4] The other four lines are in the expected position for vinyl chlorines. The nqr spectrum is fully consistant with structure VI, but not with the alternative structure V. Structure V has no chlorine atoms expected to give very high-frequency resonances; moreover, in V the four chlorines in CCl_2 groups would be expected to have (nearly) identical resonances (cf. β-C_8Cl_8, below); no such resonances are found in the spectrum of α-C_8Cl_8.

The nqr spectrum of β-C_8Cl_8 is in good agreement with the structure I proposed earlier from chemical and other spectral evidence. Resonances are found at 37.32 (1), 37.49 (1), 37.6 (2), 37.94 (2), 38.12 (1) and 38.51 (1) MHz. The lines in the narrow region 37.3-37.6 MHz are probably due to the CCl_2 chlorines.

At 180° γ-C_8Cl_8 rearranges into two further isomers: δ-C_8Cl_8, m. 86°, perhaps octachloroheptafulvene, and ϵ-C_8Cl_8, m. 111°, probably an octachlorodihydropentalene. Further studies of chemical transformation of the C_8Cl_8 isomers are in progress.

Acknowledgement. This work was partly supported by a grant from the U. S. Public Health Service--National Institutes of Health.

REFERENCES

1. A. Roedig and R. Kohlhaupt, *Tetrahedron Letters*, 1964, 1107.
2. R. Helm, Dissertation, Universität Würzburg, 1968.
3. All nqr spectra were determined using a Wilks NQR-1A spectrometer.
4. R. West and R. Martin Smith, unpublished data.
5. B. Ekström, *Chem. Ber.*, **92**, 749 (1959).
6. E. Ziegler and J. Brandmuller, *Z. Analyt. Chem.*, **210**, 193 (1965).