

infrared spectrum of the hydrochloride thus obtained was superimposable on that of 2-chloro-6-methyl-*N*-methylaniline hydrochloride, and a mixed m.p. was undepressed (210°).

1. Naegeli, C., Tyabji, A., Conrad, L. and Litwan, F. *Helv. Chim. Acta* **21** (1938) 1100.
2. Shkapenko, G., Gmitter, G. T. and Gruber, E. E. *Ind. Eng. Chem.* **52** (1960) 605.
3. Dieckmann, W. and Breest, F. *Ber.* **39** (1906) 3052.
4. Naegeli, C. and Tyabji, A. *Helv. Chim. Acta* **17** (1934) 931.
5. Naegeli, C. and Tyabji, A. *Helv. Chim. Acta* **18** (1935) 142.
6. Dahlbom, R. and Misiorny, A. *Acta Chem. Scand.* **11** (1957) 1350.

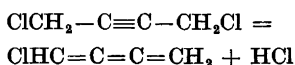
Received January 9, 1968.

Chlorobutatriene — Identification and Spectrochemical Characterization

RAGNAR VESTIN, ASTRID BORG and TORBJÖRN LINDBLÖM

Institute of Inorganic and Physical Chemistry (Catalytical Laboratory), Stockholm University, Stockholm, Sweden

Dehydrochlorination of 1,4-dichloro-2-butyne by alkali gives diacetylene¹ as an end product. Several intermediates appear in which one of the chlorine atoms is retained. We have noticed that under certain conditions a considerable amount of chlorobutatriene is formed, according to the formula



The substance can readily be purified by gas chromatography. On a di-ethyl-hexyl-sebacate column at 50°C the three substances 1,4-dichlorobutyne, chlorobutatriene, and carbon tetrachloride have the

relative delays of 21.6, 2.21, and 1.00, respectively.

The identification is primarily based on the mass spectrum obtained by using a combined gas chromatograph-mass spectrometer.² After correction for background the largest peaks are: *m/e* — rel. int.; 49—2.1; 50—30.9; 51—100.0; 52—4.4; 60—2.5; 62—1.3; 84—0.8; 85—2.7; 86—87.2; 87—6.5; 88—29.2; 89—1.7.

The occurrence of chlorine is demonstrated by the intensity relation 3:1 of the mass numbers 86:88 corresponding to the molecular ions with ³⁵Cl and ³⁷Cl. The molecular weight is consequently 86.5. The relation ¹³C:¹²C in the substance appears most evident from the intensity relation 4.4:100.0 between the mass numbers 52:51 (corresponding to the ions ¹³C₃¹³CH₃⁺ and ¹²C₃H₃⁺, respectively). Hence, the assumption of four carbon atoms is confirmed. IR- and NMR spectra provide other necessary data for the identification.

Of simple butatriene compounds only the hydrocarbon itself has been described so far, 1952 by Schubert.³ The preparation by treatment of 1,4-dibromo-2-butyne with alkali and zinc is closely related to the one described here; and there is reason to assume that bromobutatriene is formed as an intermediate.

In UV an absorption with maximum at 278—279 mμ is observed. The chlorine atom has caused a considerable bathochromic displacement — the absorption maximum³ of unsubstituted butatriene

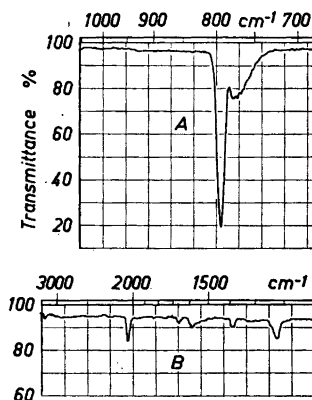


Fig. 1. IR spectrum of chlorobutatriene. Vapour mixed with He, 10 cm cell, NaCl optics, 25°C. A: Ca. 1.9×10^{-4} mole \cdot l⁻¹; B: Ca. 1.5×10^{-3} mole \cdot l⁻¹.

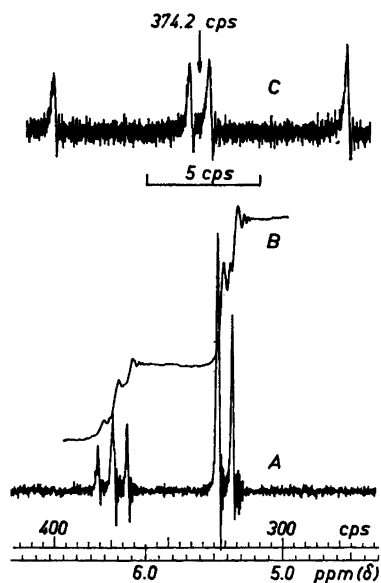
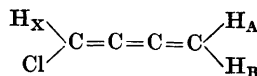


Fig. 2. NMR spectrum (60 Mc) of chlorobutatriene. 0.7 M solution in $\text{CDCl}_3/\text{CCl}_4$, 20°C .

occurs at 241μ . The IR spectrum of gaseous chlorobutatriene is given in Fig. 1 where curve A, at low concentration, shows the most intense lines at 794 cm^{-1} (ϵ ca. $380 \text{ l-mole}^{-1} \text{ cm}^{-1}$) and 780 (broad) cm^{-1} . At the same concentration other peaks can hardly be observed (noise level $\pm 1\%$) between 670 and 4000 cm^{-1} . A higher concentration gives a spectrum between 1100 and 4000 cm^{-1} , curve B, showing more absorption bands. Reliable criteria of purity are lacking but the peak at 2050 cm^{-1} no doubt belongs to the substance itself and is probably related to the characteristic allene band at 1980 cm^{-1} . There is no strong absorption between 3270 and 3205 cm^{-1} which is important in eliminating the isomeric chlorobutenyne structures.

The NMR spectrum of the substance at 60 Mc shows (Fig. 2) at lower resolution (curve A) apparently a simple A_2X case with an A_2 doublet and an X triplet; the corresponding integrals (curve B) have the relation 2:1. At high resolution we get a spectrum which, as expected, is of ABX type.



Curve C shows the splitting of the X part into an 1:1:1:1 quartet. The AB part is also split into a quartet containing two close pairs: $6.86-6.54-0.50-0.00$ (+ 322) cps. At 100 Mc the distance between the inner pair in the X quartet is decreased, and in the AB part the two pairs almost coalesce into simple lines.

The information gained does not permit a complete interpretation and experiments with spin decoupling are so far unsatisfactory (for technical reasons). Positive results are the following: $\nu_X = 374.2$ cps ($\delta = 6.23$ ppm); $\nu_{AB} = 325$ cps ($\delta = 5.42$ ppm); $|J_{AX} + J_{BX}| = 12.8$ cps; $D_+ - D_- = 0.45$.⁴ There are significant differences between J_{AX} and J_{BX} and between ν_A and ν_B but they are probably small.

One of the long range coupling constants must be ≥ 6.4 cps not far from the high value (+ 7.8) that has been predicted, but not yet confirmed, for butatriene⁵ itself on the basis of a second order perturbation treatment of the π -electron contribution. However, the coupling constant J_{AB} for the geminal hydrogen atoms cannot be of the magnitude (-9 cps) that has been predicted for allene.⁶

This work has been supported by grants to research on catalytic chemistry at the Stockholm University from the *Swedish Council for Applied Research and Knut and Alice Wallenbergs Foundation*. We wish to thank Sture Forssén for determining the NMR spectrum at 100 Mc and for stimulating discussions.

1. Pomerantz, P. *J. Res. Natl. Bur. Std.* **52** (1954) 51.
2. Ryhage, R. and Wikström, S. *Sci. Tools* **14** (1967) No. 1.
3. Schubert, W. M., Liddicoet, T. H. and Lanka, W. A. *J. Am. Chem. Soc.* **76** (1954) 1929.
4. Symbols according to Pople, J. A., Schneider, W. G. and Bernstein, M. *J. High Resolution Nuclear Magnetic Resonance*, New York 1959.
5. Karplus, M. *J. Chem. Phys.* **33** (1960) 1843.
6. Pople, J. A. and Bothner-By, A. A. *J. Chem. Phys.* **42** (1965) 1339.

Received December 29, 1967.