

crystals, m.p. 74–75 °C (lit.⁵ 75 °C). By suction of fraction 3 the oily isomer was obtained contaminated with 20 % of the solid isomer. NMR of the crystalline isomer:⁵ δ 1.53 ppm (s, 6, methyl protons), 2.15 (an AA'BB' spectrum centered at 2.15 ppm, 4, methylene protons), 7.12–7.63 (m, 10, aromatic protons). NMR of the liquid isomer:⁵ δ 1.60 ppm (s, 6, methyl protons), 2.20 (s, 4, methylene protons), 7.00–7.58 ppm (m, 10, aromatic protons). The two isomers showed identical mass spectra, m/e (% of base peak): 238(15), 237(100), 219(7), 117(21), 105(95), 91(11), 77(16), 43(15). (Found: C 85.3; H 7.97; O 6.49. Calc. for $C_{15}H_{20}O$: C 85.7; H 8.00; O 6.34).

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4-Chlorobuten-3-yne: a Spectrochemical Characterization

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True acetylenic hydrogens are generally replaced by halogen by action of alkaline hypohalites. This reaction has been applied to vinylacetylene with different halogen atoms by Carothers and Jacobson.¹ We prepared 4-chlorobuten-3-yne by adding monovinylacetylene to a potassium hypochlorite solution.

The substance was isolated and purified with gas liquid chromatography at a temperature of 100 °C. The column was packed with diethylhexyl sebacate (15 %) absorbed on Chromosorb.

The identification is primarily based on the mass spectrum obtained by using a combined GLC–MS. After correction for background, the largest peaks are: m/e (rel. intensity), 49(19.5), 50(46.5), 51(100.0), 52(4.5), 60(10.5), 62(3.5), 84(10.5), 85(12.0), 86(98.5), 87(8.5), 88(30.5) and 89(1.5).

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 and the mass numbers 60:62 probably corresponding to the ions $CHC^{35}Cl^+$ and $CHC^{37}Cl^+$. The molecular weight is consequently 86.5. The relation ¹³C:¹²C in the substance appears most evident from the intensity relation 4.5:100.0 between the mass numbers 52:51, corresponding to the ions ¹³CC₂H₃⁺ and C₂H₃⁺. Hence the assumption of four carbon atoms is confirmed.

A UV-spectrum of the substance was run between 340 and 200 nm. An absorption at 277–278 nm was observed.

For monovinylacetylene, absorption at 221 nm and 227.5 nm has been reported by Georgieff *et al.*²

The IR-spectrum of gaseous 4-chlorobuten-3-yne is given in Fig. 1. A theoretical calculation of the frequencies, from a normal coordinate analysis using a simple diagonal valence force field, shows good agreement with the obtained spectrum for some of the peaks.^{3,4}

At 3120 cm^{-1} we observed the asymmetric hydrogen stretch for the vinyl group. The peak at 3035 cm^{-1} belongs either to the symmetric hydrogen stretch for the vinyl group or a stretch of the remaining hydrogen. At 2220 cm^{-1} the characteristic stretching of $-C\equiv C-$ was observed and at 1600 cm^{-1} the $-C=C-$ stretch. There is no strong absorption around 3300 cm^{-1} which shows the purity of the substance and eliminates the isomeric chlorobutenyne structures.^{5,6}

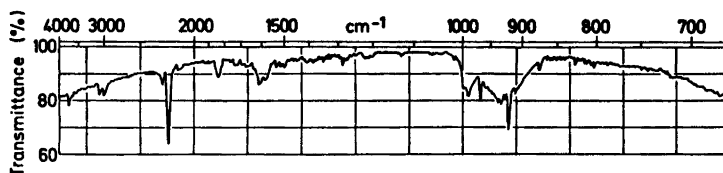


Fig. 1. IR spectrum of 4-chlorobuten-3-yne. Vapour mixed with He, 1 m cell, KBr optics. The curved background line depends on multiple reflections in the 1 m cell; no reference cell could be used.

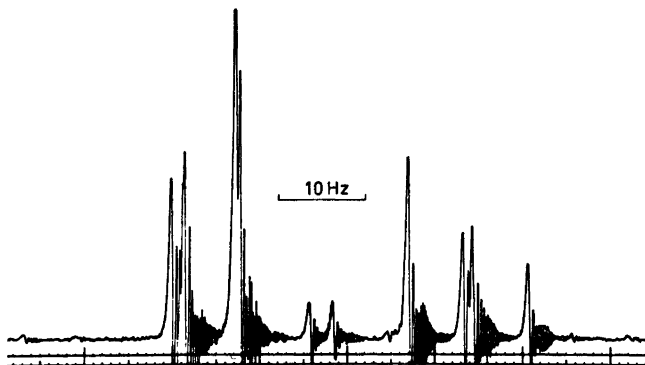


Fig. 2. High resolution NMR spectrum of 4-chlorobuten-3-yne at 98 MHz with C_6D_6 as solvent.

The NMR-spectra of 4-chlorobuten-3-yne were recorded at 60 MHz with carbon tetrachloride as solvent and at 98 MHz with deuteriochloroform and deuteriobenzene as solvents. The spectra run with CCl_4 and $CDCl_3$ as solvents showed a surprising resemblance to an A_2B spin system spectrum. With C_6D_6 as solvent a spectrum was obtained with quite a different appearance (see Fig. 2) as expected from the molecular structure. The observed thirteen lines were used in a least squares fitting procedure, LAOCN 3⁷ and the following chemical shifts and spin-spin coupling constants were obtained.

The three vinyl protons are labelled C *trans* to A and *cis* to B; $\nu_A = 534.6$ cps [$\delta_A = 5.45(5)$ ppm], $\nu_B = 507.3$ cps [$\delta_B = 5.18$ ppm], $\nu_C = 535.0$ cps [$\delta_C = 5.45(9)$ ppm], $J_{AB} = 0.9$ cps, $J_{AC} = 17.7$ cps, and $J_{BC} = 11.9$ cps.

The values of the chemical shifts are measured from TMS used as internal standard. The obtained values of the coupling constants are in good agreement with those obtained from other vinyl compounds.⁸ The chemical shift values are somewhat low, probably due to the solvent, C_6D_6 , but their relative positions are in agreement with other vinyl compounds.^{8,9}

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