

coupling between geminal protons. Systems requiring hyperconjugative structures which violate the adjacent charge rule would be the exceptions.

Acknowledgment.—This work was supported by the National Science Foundation under grant No. G-11313.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY EMORY UNIVERSITY, ATLANTA 22, GEORGIA]

Synthesis and Proton Magnetic Resonance Spectrum of Propargyl Cyanide

BY G. S. REDDY, LEON MANDELL AND J. H. GOLDSTEIN

RECEIVED APRIL 24, 1961

Propargyl cyanide has been prepared by the reaction between propargyl bromide and cuprous cyanide. The structure of the product was proved by detailed comparison of its n.m.r. spectrum with those of a series of propargyl halides and haloallenes. Further confirmatory evidence was provided by the infrared spectrum of the product. The compound was stable on standing for ten months, as shown by the persistence of its n.m.r. spectrum. It is concluded that the previously reported preparations of cyanoallene might in fact have yielded propargyl cyanide.

It is well known that acetylenic nitriles are difficult to prepare. The first unsuccessful attempts in this field were made by Johnson¹ who explained the failure as due to acetylenic-allenic isomerism.² Later, for the first time an acetylenic nitrile having at least three methylene groups between the nitrile group and the triple bond was prepared by Newman and Wotiz.³ These authors failed to obtain the nitrile by the general procedure of treating the chloride with AgCN. However, when they treated the corresponding bromide in an anhydrous medium with cuprous cyanide at 150–160°, they were able to obtain the nitrile. Some attempts have been made by German workers⁴ to synthesize acetylenic nitriles with only one methylene group between the nitrile group and the triple bond by refluxing a mixture of propargyl chloride, cuprous chloride and hydrogen cyanide. In the reaction product no chloroallene was detected. From the fact that $\text{CH}_3\text{-(CH}_2\text{)-C}\equiv\text{C-CH}_2\text{Cl}$ ($n = 2, 3$) under similar conditions gave a mixture of acetylene and allene, it was postulated that in the above reaction propargyl cyanide was first formed and subsequently rearranged to cyanoallene. This product, which was described as cyanoallene by these workers has the same boiling point and refractive index as the product we have prepared and have now shown to be propargyl cyanide. Thus, it is possible that the product previously reported as cyanoallene was in fact propargyl cyanide.

In this investigation the product of the reaction described below has been shown to be propargyl cyanide from its proton magnetic resonance (n.m.r.) and infrared spectra. It appears to be quite stable and does not undergo rearrangement on standing in a sealed tube at room temperature over a period of ten months. Since our n.m.r. proof depends upon comparisons with the spectra of other propargylic compounds, it was necessary to correct the chemical shifts of both the acetylenic and methylenic protons for the effect due to the diamagnetic anisotropy of the nitrile group. These corrections are given in detail below.

(1) A. W. Johnson, *J. Chem. Soc.*, 1009 (1946).

(2) A. W. Johnson, "Acetylenic Compounds," Vol. I, Edward Arnold and Company, London, 1946, p. 63.

(3) M. S. Newman and J. H. Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949).

(4) German Patent 1,064,504; F21, 815 (1959).

Experimental

Preparation of Propargyl Cyanide.—One hundred twenty five grams of pure propargyl bromide was refluxed with fifty grams of cuprous cyanide for 48 hr. The copper salts were filtered off and the filtrate fractionated at 50 mm. After the low boiling fraction was removed a fraction of 15 g., b.p. 45–60 (50 mm.) was collected. The pot exploded at this point of the distillation. This happened on repetition of the synthesis and is due, undoubtedly, to copper acetylides formed during the reaction and present in the crude product. The distillate was filtered, to remove carbon blown over in the explosion, and redistilled to give 12.3 g. of material boiling at 45–48 (40 mm.). This product showed in its n.m.r. spectrum a sharp and fairly strong line at the water region (–212.5 c.p.s. from tetramethyl silane internal reference in carbon tetrachloride solution) as well as a triplet and a doublet in the region of propargyl bromide with spacing equal to that in propargyl bromide. This indicated the presence of water and propargyl bromide in the product. On refractionating the product the peak presumed to be due to water reduced greatly to about 1% and the peaks assigned to propargyl bromide disappeared completely. The refractive index is $n_D^{20} = 1.4610$. The physical properties of this material (boiling point and refractive index) corresponded well with those reported by the German workers.⁴

N.m.r. Spectrum.—The spectrum was taken on a Varian Associates Model 4300B High Resolution Spectrometer operating at 40 Mc./sec. and equipped with a Flux Stabilizer. Spinning 5 mm. o.d. Pyrex glass tubes were used for sample tubes, the solvent was CCl_4 . (The product does not dissolve in inert materials such as cyclohexane or tetramethyl silane (TMS).) About 10% TMS was added to the solution to serve as internal reference. Since the sample and the reference are in the same medium, namely, CCl_4 , there is no necessity to make any bulk magnetic susceptibility corrections in order to be able to compare effectively the chemical shifts with those of the compounds included in Table II which were taken in TMS. Calibrations were made by the usual side band technique. All the chemical shifts are expressed in cycles per second from the TMS internal reference. The coupling constants are expressed directly in cycles per second. Calibrations were repeated after storing the sample in a sealed tube for ten months to see if there was any rearrangement to the corresponding allenic compound. The spectra were unchanged after this time, and hence it was concluded that propargyl cyanide is stable under the conditions of storage at room temperature and does not rearrange to cyanoallene.

Infrared Spectrum.—The infrared spectrum was taken on a Perkin-Elmer Model 21 Spectrometer with rock salt optics. Carbon tetrachloride was again used as the solvent.

Discussion

The n.m.r. spectrum of the product, shown in Fig. 1, consists of a doublet and a triplet about 45 c.p.s. apart. The pattern is that of a first order A_2X system with the A_2 protons at lower field. The coupling constants and the chemical shifts can be readily obtained from the spacings

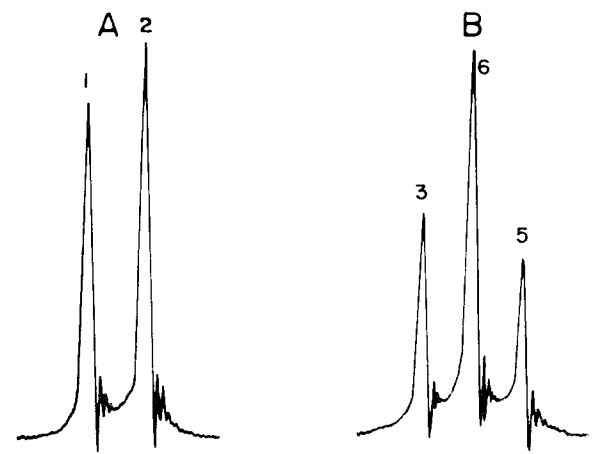


Fig. 1.—Proton magnetic resonance spectrum of propargyl cyanide in CCl_4 at 40 Mc./sec: A, methylene protons; B, acetylenic proton. The groups A and B are not drawn to the same height scale.

and the centers of each group, respectively (Table I). The n.m.r. spectral parameters thus obtained are shown in Table II. The long-range H-H coupling constants in allene and methyl acetylene (propyne) are 7.0 ± 0.1 and 2.9 ± 0.2 c.p.s., respectively.⁵ Halogen substitution in allene (haloallenes) decreases the coupling constant appreciably, from 7.0 to 6.0 c.p.s., analogous to the effect of halogen substitution in ethylene. The H-H coupling constants in ethylene, about 18 c.p.s. (*trans*) and 11 c.p.s. (*cis*)⁶ are reduced to 14–15 and 7.0–7.5 c.p.s., respectively, in the vinyl halides.⁷ However, the decrease in the coupling constants is about the same for all the halogens. On the other hand, halogen substitution at the methyl group in methyl acetylene (propargyl halides) does not produce an appreciable change in the coupling constants. This is reasonable because of the structural differences in allene and methyl acetylene, substitution being on an sp^2 hybridized carbon in the case of haloallenes and on an sp^3 hybridized carbon in the case of propargyl halides. This is in accordance with very small changes in the long-range coupling constants in 3-substituted propenes.⁸ From these facts it is not reasonable to expect that substitution by a nitrile group in allene will change the coupling constant from 7.0 c.p.s. to the observed value of 2.85 c.p.s. By this reasoning it appears that the coupling constants are those of a propargylic, rather than of an allenic system.

The chemical shift of the low-field doublet, presumably belonging to CH_2 protons, is -134.5 c.p.s. and that of the high-field triplet is -90.2 c.p.s. In the haloallenes the doublet is at higher field whereas in propargyl halides the triplet is at higher field. This is due to the large diamagnetic anisotropic shielding of the acetylenic proton arising from the $\text{C}\equiv\text{C}$ bond.^{9,10} This also sup-

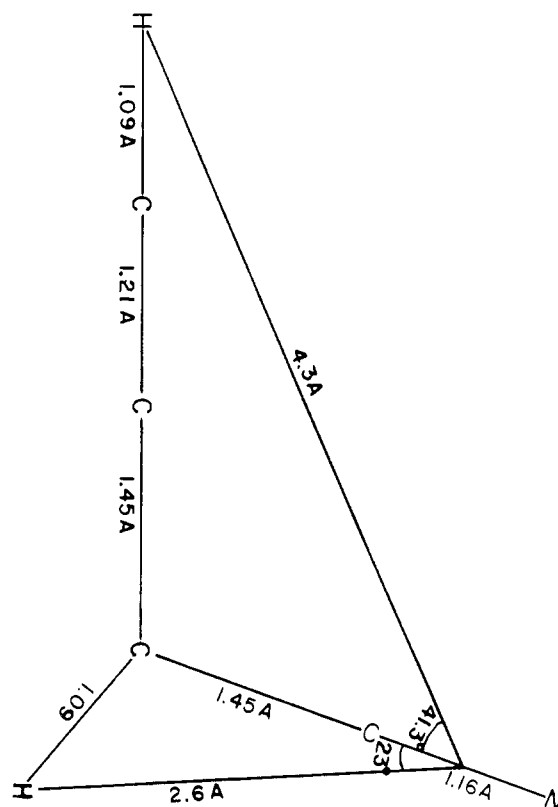


Fig. 2.—Structural parameters used for calculating diamagnetic anisotropic shielding corrections due to nitrile group in propargyl cyanide.

ports the conclusion that the product is propargyl cyanide. However, it should be remembered that the $\text{C}\equiv\text{N}$ group also gives rise to an anisotropic shielding approximately as great as that due to the $\text{C}\equiv\text{C}$ system. In acrylonitrile, for example, this effect amounts to $+45$ c.p.s. for the α -proton.¹¹ Consequently, the observed position of the triplet does not itself guarantee that the compound is propargyl cyanide.

Comparison of the chemical shifts in Table II indicates that the α -proton in chlorallene is about 48 c.p.s. at lower field than in allene. In vinyl chloride⁷ the α -proton is about 37 c.p.s. at lower field than in ethylene. If the substitution effects in ethylene¹² and allene are at least of roughly comparable magnitude, the difference of 9 c.p.s. in the ethylene protons due to nitrile substitution (the α -proton in vinyl cyanide is 9 c.p.s. below that of ethylene) leads us to predict the α -proton in cyanoallene to be at about -190 c.p.s. which is much lower than the observed value of -90.2 c.p.s. On the other hand, the difference in the α -proton shifts in vinyl chloride and vinyl cyanide, 28 c.p.s. (vinyl cyanide is at higher field before making corrections due to diamagnetic shielding arising from the $\text{C}\equiv\text{N}$ bond¹¹) indicates that the

(5) E. B. Whipple, J. H. Goldstein and W. E. Stewart, *J. Am. Chem. Soc.*, **81**, 4761 (1959).

(6) G. S. Reddy and J. H. Goldstein, unpublished values.

(7) E. B. Whipple, W. E. Stewart, G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **34**, 2136 (1961).

(8) E. B. Whipple, J. H. Goldstein and G. R. McClure, *J. Am. Chem. Soc.*, **82**, 3811 (1960).

(9) E. B. Whipple, J. H. Goldstein, L. Mandell, G. S. Reddy and G. R. McClure, *ibid.*, **81**, 1321 (1959).

(10) J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

(11) G. S. Reddy, J. H. Goldstein and L. Mandell, *J. Am. Chem. Soc.*, **83**, 1300 (1961).

(12) G. S. Reddy and J. H. Goldstein, *ibid.*, **83**, 2040 (1961).

TABLE I
OBSERVED N.M.R. SPECTRUM OF PROPARGYL CYANIDE

Peak no.	Frequency (in c.p.s.) in CCl ₄ , from TMS internal reference
1	-135.8
2	-132.9
3	-93.0
4	-90.15
5	-87.3

(B) (A)
H—C≡C—CH₂CN. $\omega_A = -134.35$ c.p.s. $\omega_B = -90.2$
c.p.s. $J_{AB} = 2.85$ c.p.s.

TABLE II
N.M.R. SPECTRAL DATA FOR HALOALLENES AND PROPARGYL
HALIDES

	CH ₂ ^a	—CH ^a	J_{H-CH_2} ^b	Ref.
H ₂ C=C=CH ₂	-182.0	7.0 ± 0.1	1
H ₂ C=C=CHCl	-201.9	-230.3	$6.1 \pm .1$	9
H ₂ C=C=CHBr	-193.1	-233.9	$6.1 \pm .1$	9
H ₂ C=C=CHI	-178.7	-225.1	$6.3 \pm .1$	9
H—C≡C—CH ₃	-65.0	-60.0	$2.9 \pm .2$	7
H—C≡C—CH ₂ Cl	-157.1	-89.5	2.8	7
H—C≡C—CH ₂ Br	-147.3	-89.6	2.8	7
H—C≡C—CH ₂ I	-140.7	-87.7	2.8	7
H—C≡C—CH ₂ CN ^c	-134.4	-90.2	2.85	
	(-182.0)	(-92.0)		

^a All the values are in c.p.s. at 40 Mc./sec. with respect to tetramethyl silane internal reference. ^b In c.p.s. ^c The values in the parentheses are after making the necessary corrections for anisotropic shielding of the nitrile group.

α -proton chemical shift in cyanoallene will be at about -200 c.p.s. which again is much too low compared with the observed value of -90.2 c.p.s. This clearly suggests that the triplet is most likely due to an acetylenic rather than allenic proton.

The doublet is about 23 c.p.s. above that in propargyl chloride, which is about the same as the difference between vinyl chloride and cyanide. From the electronegativity of the nitrile group and of chlorine, one would expect the protons attached to the carbon atom bearing the nitrile group to be at lower field than in the chlorine analog. This has been clarified in vinylic systems by calculating the diamagnetic anisotropic shielding corrections due to the nitrile group on the α -protons.¹¹ Similar calculations using the structural parameters shown in Fig. 2 gave corrections of -47.6 c.p.s. and -1.8 c.p.s. for the CH₂ and \equiv CH protons, respectively, in propargyl cyanide. After making these corrections, the chemical shifts of

CH₂ and CH are -182.0 and -92.0 c.p.s., both of which are at lower field than the corresponding values in propargyl chloride. These corrected values are in the same order and of the magnitude expected from the electronegativities of nitrile and chlorine and upon comparison with vinyl chloride and cyanide.

The infrared spectrum of this product in CCl₄ gave a strong and sharp band at 3 μ which is a characteristic \equiv C—H stretching frequency. It also showed a broad, strong band at about 15 μ which is a characteristic \equiv C—H bending frequency. Besides these, it contains a band at 4.4 μ and another at 4.65 μ which can be assigned to the C \equiv N and C \equiv C stretching frequencies, respectively. However, there is a fairly strong band at 5.05 μ which is in the general region of a characteristic allenic stretching frequency. The presence of this band is somewhat difficult to explain. It might be either a combination or overtone band, or there might conceivably be such rapid exchange between the allenic and propargylic system that only infrared can detect both the species simultaneously. (N.m.r. spectra, because of their relatively low frequency, cannot reveal both the forms if the exchange is too rapid but gives instead an average spectrum of the two forms.) However, if the exchange is too rapid to be detectable by n.m.r., the spin-spin coupling effects would be expected to smear out and hence the spectrum should consist of broad rather than sharp and highly resolved peaks. Also, if this were the case, the chemical shifts would be expected to occur somewhere between those of propargyl cyanide and cyanoallene. The above arguments and evidence completely rule out this exchange and prove beyond doubt that the only species present is propargyl cyanide. Hence, it is felt that the infrared band at 5.05 μ is probably a combination or overtone band.

In summary, this investigation has shown that the synthetic procedure described above produces propargyl cyanide and that, contrary to previous reports, this compound does not rearrange to cyanoallene.

Acknowledgments.—The authors wish to thank Miss Joan Terry Ward for assistance with the synthesis of propargyl cyanide. They are indebted to the National Institutes of Health for a grant (A-2397 (c-2)) in partial support of this work.