et al.,[3] suggested that this unexpected result could be explained if there was a decrease in the barrier to torsional motion of the methyl group on deuterium substitution in the initial state and that this barrier became small in the transition state. In a more detailed theoretical analysis, Bartell[5] discussed the possibility that α and β secondary deuterium isotope effects could arise from changes in nonbonded interaction accompanying the change from tetrahedral to trigonal configuration.

Wolfsberg and Stern[6] have shown that large normal temperature-independent isotope effects for such reactions can be calculated if force constants, which give rise to small frequencies (such as torsions), become larger in the transition state, and some large force constants (*e.g.*, C–H stretching) simultaneously become smaller. Since the un-ionized isopropyl halides do not interact strongly with the solvent, nucleophilic interaction could provide just such a condition in the activation process for solvolytic displacement by an SN2 mechanism. However, in addition to uncertainties with regard to the extent of such interaction and with respect to the degree of charge development, there must be added the possibility of anharmonicity, of tunnelling, and of possible variation in the transmission coefficient.

These kinetic uncertainties are in some measure removed and the position for argument and discussion of this surprising phenomena materially strengthened by the discovery that the secondary deuterium isotope effect for the thermodynamic dissociation constants in acid–base equilibria involving mono- and dimethylamine are temperature independent over 30–40° temperature range (Table I).

TABLE I

K_D/K_H FOR BASE IONIZATION OF MONO- AND DIMETHYLAMINES IN WATER

	K_D/K_H	
T, °C.	Monomethylamine	Dimethylamine
5	1.14	
10		1.32
15	1.16	1.32
20		1.31
25	1.12, 1.13	1.31
30		1.31
35	1.14	1.32
40		1.33
45	1.13	

The deuterated compounds were better than 97% $-d_3$ and $-d_6$, respectively. Equilibrium values were obtained by a conductance method adapted from that described by Ives and Pryor.[7] The concentration of amine was in the range 0.003–0.007 mole/l.

Everett and Wynn-Jones[8] report $K_B = 0.0004246$ for monomethylamine at 25°. We found 0.0004517. For dimethylamine the corresponding values are 0.0005954 and 0.000604. Since the potentiometric method is expected to give low values of K_B,[7] the difference is probably not important.

The solvated methylammonium ion is not a good model for the transition state in the solvolysis of secondary halides but it will be obvious that the same type of calculation proposed by Wolfsberg and Stern[6] will be expected to yield similar temperature-independent isotope effects for amine equilibria provided suitable changes in force constants are assumed.[9]

In this connection it is significant that MacLean and Leffek[10] have recently reported that the *inverse* isotope effect associated with the displacement of I^- from methyl iodide by amines in benzene is temperature independent.

(5) L. S. Bartell, *J. Am. Chem. Soc.*, **83**, 3567 (1961).
(6) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 325 (1964).
(7) D. J. G. Ives and J. H. Pryor, *J. Chem. Soc.*, 2104 (1955).
(8) D. D. Everett and W. F. R. Wynne-Jones, *Proc. Roy. Soc.* (London), **A177**, 499 (1941).
(9) M. Wolfsberg, private communication.
(10) J. W. MacLean and K. T. Leffek, Spring Meeting, C. I. C. Kingston, 1964.
(11) National Research Council of Canada Postdoctoral Fellow 1961–1963.

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Cyanogen Azide

Sir:

Cyanogen azide (1) has been synthesized in virtually quantitative yield from the reaction of sodium azide with cyanogen chloride in aprotic media.[1] This new

$$NaN_3 + ClCN \longrightarrow \underset{1}{N_3CN} + NaCl$$

azide has a versatility and scope of chemical reactivity that is very broad and useful.

Cyanogen azide, a colorless oil, detonates with great violence when subjected to mechanical or thermal shock, and *great care should be taken in any work with this compound.* It can be handled relatively safely in solvents where most of its properties have been studied. The half-life of a 27% solution of the azide in acetonitrile is 15 days at room temperature, but this solution can be stored indefinitely without change at 0 to −20°. The pure azide is too sensitive for combustion analysis; however, its molecular weight (freezing point in benzene) is 69 (calcd. 68).

The infrared spectrum of 1 in carbon tetrachloride shows absorptions at 2240 (s), 2199 (vs), 2143 (s), and 2090 (s) cm.$^{-1}$ (associated with the nitrile and azide stretching vibrations) and at 1245 (vs) cm.$^{-1}$ (C–N stretching). In cyclohexane, 1 has two resolved absorptions at 275 (ϵ 103) and 220 mμ (ϵ 2157). The mass spectrometric cracking pattern of . shows a peak of 48% relative abundance for the parent and is entirely consistent with the formulated structure.

The synthesis of cyanogen azide is carried out by adding cyanogen chloride to sodium azide. Excess cyanogen chloride or anhydrous aprotic solvents may be used as reaction media. In a typical preparation, sodium azide was suspended in dry acetonitrile, and cyanogen chloride was distilled into the mixture at a rate to maintain the temperature below 12°. The solution was allowed to warm to room temperature and filtered to remove sodium chloride. The use of dry solvents is important to avoid the formation of explosive, solid by-products, and care also must be taken

(1) There are several references to cyanogen azide in the older literature, none of which appear correct. For example, M. G. Darzens [*Compt. rend.*, **154**, 1232 (1912)] obtained a crystalline product incorrectly characterized as N_3CN, which was later suggested by C. V. Hart [*J. Am. Chem. Soc.*, **50**, 1922 (1928)] to be guanyl azide, a result we have now confirmed.

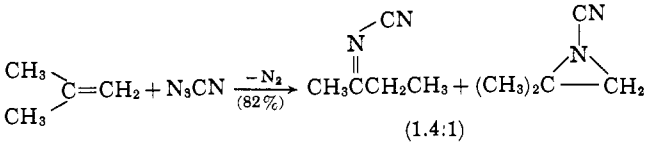
to avoid separating cyanogen azide from solution through evaporating low-boiling solvents, cooling saturated solutions, or freezing the solvent.

Cyanogen azide behaves principally as a highly reactive organic azide. It is reduced by hydrogen sulfide to cyanamide in 80% yield, and with triphenylphosphine 1 forms N-cyanotriphenylphosphinimide **2**, m.p. 193–195°, in 88% yield.

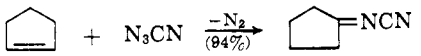
$$N_3CN + H_2S \longrightarrow H_2NCN + S + N_2$$

$$N_3CN + (C_6H_5)_3P \longrightarrow (C_6H_5)_3P{=}NCN + N_2$$

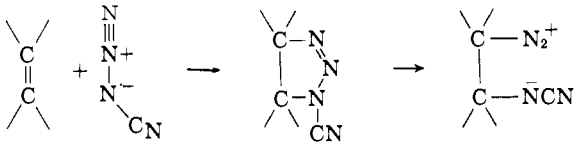
Cyanogen azide reacts rapidly with olefins at 0–35° to form alkylidene cyanamides and/or N-cyanoaziridines. The following examples illustrate the reaction.



(1.4:1)



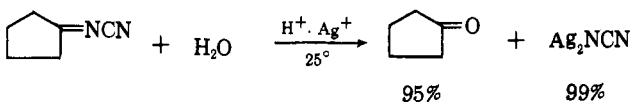
In all cases, the cyano-bearing nitrogen is found on the most highly substituted carbon of the olefin, and mechanism studies, including reaction kinetics, indicate that the rate-determining step is concerted addition of the polarized, electron-deficient azide group to the double bond to form an unstable triazoline **3**. The products and product ratios can be interpreted in terms of carbonium ion intermediates believed to arise *via* the zwitterion **4**. The reaction is potentially of con-



3 **4**

siderable mechanistic interest since it resembles the Tiffeneau–Demjanov reaction and may present the opportunity to study the behavior of aliphatic diazonium ions in aprotic media.

The alkylidene cyanamides are rapidly hydrolyzed by aqueous acid at room temperature to ketones and cyanamide, and the reaction is facilitated by silver ion, *e.g.*



95% 99%

This new ketone synthesis occurs without further rearrangement and is general.

Complete details on the chemistry of cyanogen azide will be published later.

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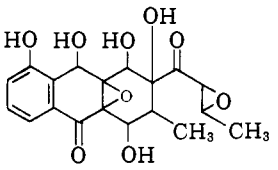
RECEIVED AUGUST 26, 1964

The Structure of Cervicarcin

Sir:

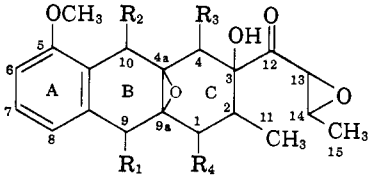
Cervicarcin[1] is an antitumor antibiotic[2] produced by *Streptomyces ogaensis*.[3] We wish to present evidence which enables the assignment of structure I to cervicarcin.



I

Cervicarcin, $C_{19}H_{20}O_9$, m.p. 205°, $[\alpha]^{26}D$ −59.7° (*c* 1.4, ethanol), is monophenolic (pK_a' 9.0 in 60% ethanol) and converted with diazomethane into methylcervicarcin (II), $C_{20}H_{22}O_9 \cdot 0.5H_2O$, m.p. 227°, ν^{KBr} 1720 and 1693 cm.$^{-1}$. The ultraviolet spectrum of cervicarcin, λ_{max}^{EtOH} 227, 264, and 323 mμ (ε 14,700, 7860, and 3700), was superimposable with that of 5-hydroxytetralone.[4] II was acetylated with acetic anhydride and sodium acetate to furnish a triacetate (III), $C_{26}H_{28}O_{12}$, m.p. 256°. The n.m.r. spectrum ($CDCl_3$)[5] showed the presence of three acetyl groups at δ 1.65, 2.04, and 2.11, and one hydroxyl at δ 3.61, indicating that four hydroxyls must be present in the molecule.

The n.m.r. spectra of cervicarcin were measured in pyridine and acetone solutions. In the latter solution absorptions of protons at 1, 4, and 10 positions are further split into AB types[6] as compared with those in pyridine, which disappeared upon adding a trace of acid, and which shifted to lower field upon acetylation,[7] indicating that those protons are attached to carbons bearing hydroxyl groups. Spin-decoupling experiments established relationships between ten hydrogens in cervicarcin; upon double irradiation at 14-H and at 2-H, multiplicity changes of 15-CH_3 (d → s) and 13-H (d → s), and of 11-CH_3 (d → s) and 1-H (d → s), respectively, were observed. The n.m.r. data afforded strong evidence for the proposed structure which was supported by the following additional chemical evidence.



II, R_1 = O, R_2 = R_3 = R_4 = OH
III, R_1 = O, R_2 = R_3 = R_4 = $OCOCH_3$
IV, R_1 = R_2 = R_3 = R_4 = OH
V, R_1 = R_2 = O, R_3 = R_4 = OH

(1) (a) K. Ohkuma, J. Nagatsu, C. Itakura, S. Suzuki, and Y. Sumiki, *J. Antibiotics, (Tokyo), Ser. A*, **15**, 152 (1962); (b) K. Ohkuma, S. Suzuki, C. Itakura, T. Sega, and Y. Sumiki, *ibid.*, **15**, 247 (1962).

(2) C. Itakura, T. Sega, S. Suzuki, and Y. Sumuki, *ibid.*, **16**, 231 (1963).

(3) J. Nagatsu, T. Sega, S. Suzuki, and Y. Sumiki, *ibid.*, **16**, 203 (1963).

(4) The sample of 5-hydroxytetralone was kindly supplied by Dr. Y. Ohkura, Faculty of Medicine, Kyushu University.

(5) N.m.r. spectra were measured at 60 Mc.; shifts are expressed as δ-values (p.p.m.) from tetramethylsilane as internal standard; coupling constants (*J*) are expressed in c.p.s.

(6) O. L. Chapman, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

(7) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 55.