

due to Varian Associates and Mr. E. Pier for obtaining the 32.1-Mc. B¹¹ n.m.r. spectrum.

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RECEIVED JUNE 6, 1964

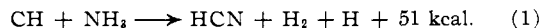
The Reaction of CH Radicals with Ammonia¹

Sir:

The reactions of active nitrogen with hydrocarbons have been carefully studied by Winkler and others² who found that, generally, the major nitrogen-containing product was HCN. Although the quantitative aspects of HCN formation in these reactions have been widely investigated, it is still in doubt whether N atoms are the sole reactive species, or if metastable N₂ molecules play a role.

As a part of his basic investigations of hydrocarbon reactions with active nitrogen, Winkler³ added NH₃ upstream from the C₂H₄ reaction flame. Instead of observing a possible decrease in HCN production, as expected, a slight increase was found. He attributed this increase in HCN production to efficient "poisoning" of the vessel walls against N-atom recombination,⁴ the slightly higher N-atom concentration leading to increased HCN formation.

We also added NH₃ upstream from some hydrocarbon-active nitrogen flames, in experiments analogous to those of Winkler. However, when we added NH₃ upstream from the C₂H₂ reaction flame (pressure ~0.25 mm. and linear velocity ~10 m./sec.), NH₃ was substantially consumed and H₂ and HCN were produced (in addition to that formed without NH₃).⁵ Without NH₃ about 10% of the N atoms present (as measured by titration with NO)^{6,7} formed HCN. Upon addition of NH₃, the formation of HCN increased by about 50% while the equivalent amount of NH₃ was consumed. In addition, sufficient H₂ was produced to suggest the following reaction.



The products were analyzed by means of a CEC 21-130 mass spectrometer whose leak was located just below the flame zone. In order to confirm our experimental results, the study of this reaction was repeated in another system, at pressures of about 1 mm., using a Bendix Model 12 time-of-flight mass spectrometer for the analyses; the same increase of HCN was found.

(1) The research reported in this document has been sponsored in part by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-174-63 and in part by the National Aeronautics and Space Administration under NSG-100-60 and NSG-158-61.

(2) References for these studies are too numerous to list here; however, see, for example, H. G. Evans, G. R. Freeman, and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

(3) C. A. Winkler and H. I. Schiff, final report to the Geophysics Research Directorate, Air Force, Cambridge Research Laboratories, Bedford, Mass., Project 4984. ARPA 42, under Contract No. AF19(604)-5979, May, 1962, p. 26.

(4) See ref. 3, p. 40.

(5) As a point of interest, we would like to mention that we were able to produce a stream of metastable N₂(A²Σ_u⁺) molecules by means of surface-catalyzed excitation (to be published) and found that, surprisingly, no decomposition of NH₃, or formation of H₂, was observed when NH₃ was added to this stream.

(6) G. B. Kistiakowsky and G. G. Volpi, *J. Chem. Phys.*, **27**, 1141 (1957).

(7) P. Harteck, R. R. Reeves, and G. Mannella, *ibid.*, **29**, 608 (1958).

An estimate of the rate of reaction, calculated from the length of the flame zone and the corresponding time of reaction, shows that the consumption of NH₃ is quite fast and that the specific rate coefficient must be at least $k_1 = 10^{-13}$ cc./particle sec.) for the above reaction.

If reaction 1 is actually responsible for the increased HCN formation, it should be possible to react NH₃ with CH radicals in the absence of N atoms. It is known that CH radicals are produced in the reactions of hydrocarbons with O atoms⁸ and, under favorable conditions, H atoms also react with hydrocarbons giving small amounts of CH radicals.⁸ Therefore, CH radicals were produced by reacting O or H atoms with C₂H₂, and addition of NH₃ to the flame zones of these reactions resulted in the production of HCN in the absence of N atoms. These findings strongly support the proposed consumption of NH₃ and formation of HCN by reaction 1. Without hydrocarbons present, at our low pressures and high pumping velocity, NH₃ was not attacked by either N or H atoms, and only slightly by O atoms.

Alternative reactions of NH₃ with C₂H, CH₂, CH₃, and other radicals have been considered, but all of these appear unlikely because of energetic, geometric, or spin considerations.

(8) A. G. Gaydon, "Spectroscopy of Flames," Chapman and Hall, London, 1957, p. 252.

(9) This paper is taken in part from a thesis by D. R. Safrany submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Department of Chemistry, at Rensselaer Polytechnic Institute.

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RECEIVED MAY 27, 1964

Optical Rotatory Dispersion of Carbohydrates¹

Sir:

The study of optical rotatory dispersion has recently been facilitated by the commercial availability of instruments capable of continuously measuring the optical rotation down to 185 mμ. This communication reports studies on the rotatory dispersion of several simple sugars and derivatives thereof, measured on a Cary Model 60 recording spectropolarimeter. The study was initiated to see if information relating to the conformation of carbohydrates in solution could be obtained from such measurements.

Figure 1 shows dispersion curves for D-glucose and D-sorbitol. It is seen that no Cotton effect is visible down to 190 mμ. This result is consistent with ultraviolet absorption data, which show no absorption peaks in this region.² An earlier report by Foster and Rao³ that glucose and sorbitol exhibit Cotton effects near 220 mμ appears to be in error.⁴

Curves of an identical nature but of different rotational magnitudes were also obtained for D-allose,⁵ D-mannose, 2-amino-2-deoxy-D-glucose, 2-deoxy-D-glucose, L-rhamnose, D-glucose 6-phosphate, α-D-glucosyl

(1) This work was supported by grants A 2903(C-5) and AM-04576 from the National Institutes of Health, U. S. Public Health Service.

(2) G. O. Phillips and P. Barber, *J. Chem. Soc.*, 3990 (1963).

(3) V. S. R. Rao and J. F. Foster, *Nature*, **200**, 570 (1963).

(4) J. F. Foster (personal communication) has confirmed the absence of Cotton effects for these compounds.

(5) We are indebted to Dr. N. K. Richtmeyer of the National Institutes of Health for this material.

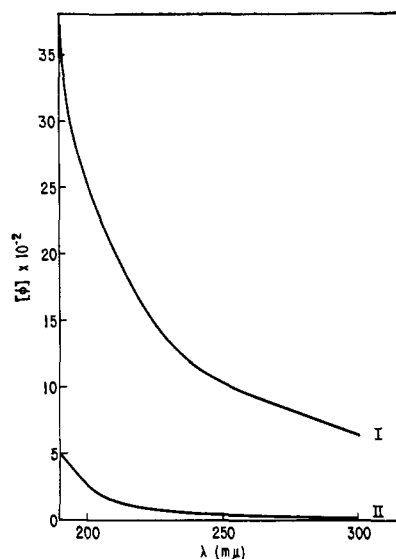


Fig. 1.—Dispersion curves for D-glucose (I) and D-sorbitol (II), in H₂O at 25°. The ordinate in this and subsequent figures is the molecular rotation, as defined by Djerassi.¹⁰

1-phosphate,⁶ α -methyl D-glucopyranoside, β -methyl D-xylopyranoside, D-ribose, D-lyxose, sucrose, and L-idose.⁷

The only aldohexoses examined which did not show plain dispersion curves were D-galactose and D-talose.⁸ The curve for galactose is illustrated in Fig. 2. As indicated in the figure, this sugar shows plain dispersion immediately after dissolving but when equilibrium in the mutarotation reaction has been reached the curve shows a maximum at about 208 m μ . We are not able to determine if this is the maximum of the first peak of a positive Cotton effect or the beginning of a negative Cotton effect having a maximum at some lower wave length. The reason for this effect is not known at present but might arise from the furanoside form known to be present in sugars of the galacto configuration. Furanosides such as sucrose or 1,2-isopropylidene-D-glucofuranose did not exhibit this effect but are not appropriate models. Alternatively, the observed effect may be the result of rotational cancellations which are inherent in this particular configurational isomer. Talose shows a similar curve with a lower magnitude of rotation. Also included in Fig. 2 is the dispersion curve for L-fucose which is essentially the mirror image of the D-galactose curve. This is the expected result since the contribution of C-6 to the optical rotation should be relatively small.

In compounds such as D-ribose and 2-deoxy-D-glucose where substantial amounts of open chain form are present, a Cotton effect might be expected above 200 m μ where the $n \rightarrow \pi^*$ transition occurs, but none were observed, possibly because the free aldehyde is completely hydrated. However, whenever a carboxyl or acyl group was present in the molecule, either in the chain or at the terminal carbons, a Cotton effect was observed as indicated by the curves in Fig. 3. Cotton effects were also observed in this region of the spectrum

(6) Curves of an identical shape and differing only slightly in magnitude were obtained at pH 7 and pH 1.

(7) Prepared from crystalline 1,2-O-isopropylidene-L-idofuranose by hydrolysis with Dowex 50 H⁺ resin. The sample was chromatographically homogeneous and contained no L-idosan.

(8) We are indebted to Dr. H. S. Isbell of the National Bureau of Standards for this material.

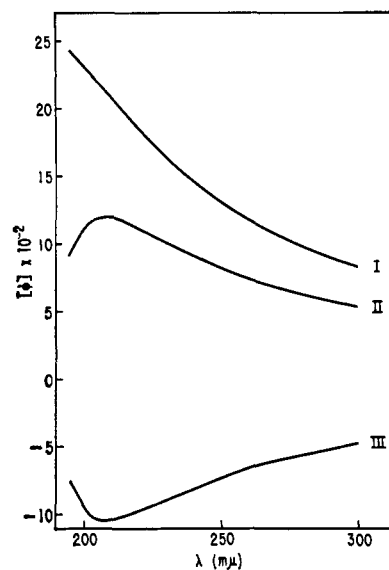


Fig. 2.—Dispersion curves for D-galactose, 10 min. after preparation of the solution (I), D-galactose at equilibrium (II), and L-fucose at equilibrium (III). All data were obtained in H₂O at 25°.

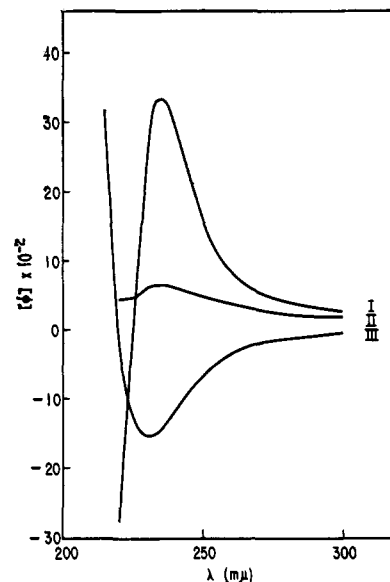


Fig. 3.—Dispersion curves for D-glucuronolactone in H₂O (I), β -D-glucose pentaacetate in methanol (II), and D-gluconolactone in H₂O (III), all at 25°.

for glucuronic acid, gluconic acid, N-acetylglucosamine, and several sugar lactones.⁹ The wave lengths of the observed effects corresponded quite closely to absorption maxima. The octant rule¹⁰ was found to be successful in predicting the sign of the Cotton effect curves from the configuration of the hydroxyl groups in the lactones studied.

Optical rotatory dispersion curves in the ultraviolet should be of general utility in providing conformational information and as a means of obtaining adequate rotational data for compounds such as sugar alcohols which have rotations of low magnitude at the sodium D-line but have very substantial rotations in the ultra-

(9) The results obtained with the lactones confirm those independently observed by S. Okuda, T. Sato, and A. Kiyomoto (A. Kiyomoto, personal communication).

(10) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960.

violet.¹¹ As an indication of the conformational information which can be obtained the following two examples can be cited. The fact that L-idose exhibits a curve nearly superimposable on that for D-glucose suggests that the predominant conformer for this sugar in aqueous solutions is C-1, since other L-sugars which have been examined show curves which are mirror images of their corresponding D-isomers. Secondly, we have recently observed that α -L-idose pentaacetate, indicated by nuclear magnetic resonance spectroscopy to be in the 1-C conformation, gave a Cotton effect curve opposite to that of β -D-glucose pentaacetate, thus confirming the n.m.r. results. Since these results were obtained on less than 1 mg. of material, the advantages are obvious.

All compounds giving plain dispersion curves followed a simple Drude equation with λ_c varying between 130 and 175 $m\mu$ in agreement with previously reported values.^{1,10}

(11) T. H. Harris, E. L. Hirst, and C. E. Wood, *J. Chem. Soc.*, 2108 (1932).

(12) Predoctoral Fellow of the National Institutes of Health, U. S. Public Health Service.

(13) Research Career Awardee of the National Institutes of Health, U. S. Public Health Service.

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RECEIVED MAY 15, 1964

The Biosynthesis of Azetidine-2-carboxylic acid

Sir:

Azetidine-2-carboxylic acid (II) was first isolated from *Convallaria majalis* (lily of the valley)^{1,2} and is fairly widely distributed in the *Liliaceae*. Attempts to determine the precursors of this unusual imino acid have so far failed. The azetidine-2-carboxylic acid isolated from *C. majalis* leaves which were fed aspartic acid or α,γ -diaminobutyric acid, uniformly labeled with C¹⁴, had negligible activity.^{3,4} Since spermidine has been shown to arise by the nucleophilic attack of 1,4-diaminobutane on S-adenosylmethionine,⁵ it was considered that azetidine-2-carboxylic acid may be formed by the intramolecular displacement of thiomethyladenosine by the α -amino group of S-adenosylmethionine (I) as illustrated in Fig. 1.

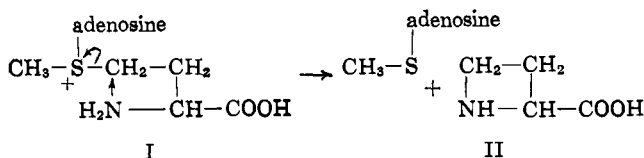


Fig. 1.—Hypothetical biosynthetic scheme for azetidine-2-carboxylic acid.

Experiments have now been carried out to test this hypothesis. DL-Methionine-carboxyl-C¹⁴ (9.32 mg., 0.2 mc.) dissolved in 20 ml. of water was administered to 20 *C. majalis* plants growing in soil out of doors

(1) L. Fowden, *Nature*, **176**, 347 (1955); *Biochem. J.*, **64**, 323 (1956).

(2) A. I. Virtanen and P. Linko, *Acta Chem. Scand.*, **9**, 551 (1955); A. I. Virtanen, *Nature*, **176**, 989 (1955).

(3) L. Fowden and M. Bryant, *Biochem. J.*, **71**, 210 (1959).

(4) P. Linko, *Acta Chem. Scand.*, **12**, 101 (1958).

(5) H. Tabor, S. M. Rosenthal, and C. W. Tabor, *J. Biol. Chem.*, **233**, 907 (1958).

(May) by means of cotton wicks inserted through the leaves near to ground level. One week after feeding the tracer, the leaves and roots (fresh weight 2.4 kg.) were harvested and azetidine-2-carboxylic acid (1.45 g., 5.0×10^5 d.p.m./mmole), aspartic acid (0.303 g., 2.0×10^4 d.p.m./mmole), and glutamic acid (0.491 g., 1.2×10^4 d.p.m./mmole) were isolated from the amino acid fraction by ion-exchange chromatography as previously described.¹ The radioactive azetidine-2-carboxylic acid was decarboxylated by heating with ninhydrin,⁶ the evolved carbon dioxide being collected and assayed as barium carbonate (4.7×10^5 d.p.m./mmole). This result indicates that essentially all the activity of the azetidine-2-carboxylic acid was located on the carboxyl group and strongly supports the new hypothesis. It is of course conceivable that the methionine is metabolized *via* homoserine to aspartic- β -semialdehyde, and then to the imino acid, as suggested by Fowden.¹ However, the low incorporation of tracer into aspartic acid (0.010%), compared with the incorporation into azetidine-2-carboxylic acid (1.67%), is not consistent with this metabolic sequence.

Acknowledgment.—The author thanks the National Science Foundation for a research grant GB-363 which supported this investigation, and his wife for allowing him to experiment with her plants.

(6) S. P. Colowick and N. O. Kaplan, "Methods in Enzymology," Vol. IV, Academic Press, Inc., New York, N. Y., 1957, p. 711.

(7) Alfred P. Sloan Fellow, 1962-1965.

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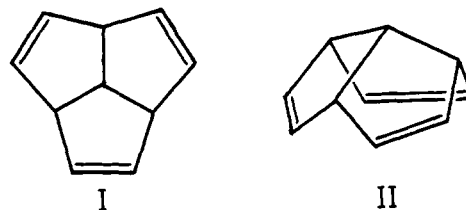
EDWARD LEETE⁷

RECEIVED JUNE 17, 1964

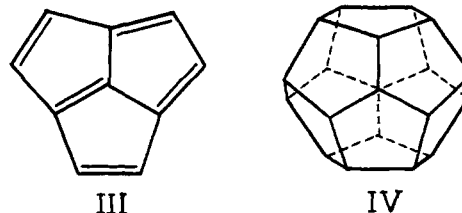
Triquinacene

Sir:

The hitherto unknown hydrocarbon, tricyclo[5.2.1-0^{4,10}]deca-2,5,8-triene (I \equiv II), here designated triquinacene, possesses three double bonds so situated in



fixed positions as to provide valuable information about the postulated phenomenon of homoaromaticity¹ and about the nature and extent of homoallylic participation in olefinic reactivity. A study of the capacity of triquinacene to form metal complexes would also be of special interest, and its possible roles as a precursor of acepentylene (III)² and of dodecahe-



(1) S. Winstein, *J. Am. Chem. Soc.*, **81**, 6524 (1959); cf. also P. Radlick and S. Winstein, *ibid.*, **85**, 343 (1963), and K. G. Untch, *ibid.*, **85**, 345 (1963).

(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 90, 290.