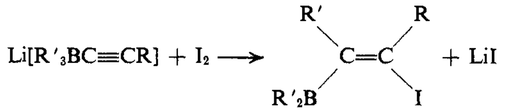
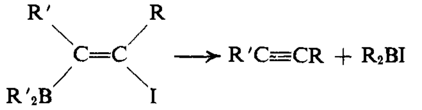
the acetylide. The lithium acetylide solution was then transferred into the 500-ml flask. The reaction solution was cooled to −78° and a solution of 7.87 g (31 mmol) of iodine in 75 ml of ethyl ether was added through the dropping funnel over a 0.5-hr period with efficient stirring. After an additional 45 min at −78°, the reaction mixture was allowed to warm to room temperature. The solution was then twice washed with 20 ml of 3 *N* sodium hydroxide (containing 1 ml of saturated sodium thiosulfate to remove residual iodine). The aqueous phase was extracted with 25 ml of ether. The combined organic phase was then treated with 32 ml of 3 *N* aqueous sodium hydroxide[5] followed by the dropwise addition of 10.5 ml of 30% hydrogen peroxide to oxidize the borinic acid by-product. Saturation of the aqueous phase with potassium carbonate yielded an organic phase in which glpc analysis revealed a 94% yield of product. The organic layer was separated, dried over potassium carbonate, and distilled. There was obtained 4.04 g (83%) of 1-phenyl-3,3-dimethyl-1-butyne, bp 100° (20 mm), $n^{20}\text{D}$ 1.5175 (lit.[6] bp 84° (10 mm), $n^{20}\text{D}$ 1.5230).

The reaction may be considered to be related to the Zweifel synthesis of cis olefins *via* the treatment of vinyldialkylboranes with iodine in the presence of alkali.[4] In the case of the vinyldialkylboranes, an iodonium species has been postulated as an intermediate in the transfer of an alkyl group from boron to carbon.[4] Such an intermediate is less probable for acetylenes, and we have no evidence requiring such a species in the present case. Electrophilic attack of iodine on the triple bond would presumably introduce a partial positive charge on the acetylenic carbon atom adjacent to the boron atom. Migration of the group from boron to the electron deficient carbon atom would produce the β-iodovinylborane (eq 7), postulated to be an intermediate. Such derivatives are known to undergo dehaloboration readily.[7] Such a dehaloboration would give the observed product (eq 8).



$$\text{Li[R}'_3\text{BC}\equiv\text{CR]} + \text{I}_2 \longrightarrow (\text{R}'_2\text{B})(\text{R}')\text{C}=\text{C}(\text{R})(\text{I}) + \text{LiI} \qquad (7)$$



$$(\text{R}'_2\text{B})(\text{R}')\text{C}=\text{C}(\text{R})(\text{I}) \longrightarrow \text{R}'\text{C}\equiv\text{CR} + \text{R}_2\text{BI} \qquad (8)$$

Probably the most general method previously available for the synthesis of acetylenes involves the reaction of alkali metal acetylides with organic halides or sulfates.[8] However, this synthesis is really satisfactory only for alkyl groups which readily undergo nucleophilic substitution reactions. The present synthesis is free of this limitation. Secondary and aryl groups appear to be introduced as easily as primary groups. Consequently, the present synthesis provides a range of applicability far broader than the procedures previously available.

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[5] In the case of aromatic boranes, 3 mol of base per mol of borinic acid is used to neutralize the phenol and the boric acid. In the case of aliphatic boranes, only 1 mol of base per mol of intermediate is adequate for the oxidation.

[6] B. S. Kupin and A. A. Petrov, *Zh. Obshch. Khim.*, **31**, 2958 (1961).

[7] J. J. Eisch and L. J. Gonsior, *J. Organometal. Chem.*, **8**, 53 (1967).

[8] C. A. Buehler and D. E. Pearson, "Survey of Organic Synthesis," Wiley-Interscience, New York, N. Y., 1970.

[9] Graduate research assistant on Grant No. GM 10937 from the National Institutes of Health. Partial assistance provided by a cooperative research program under NSF Grant No. GP 27742X is also acknowledged.

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A Novel Ring Contraction of $O^{5'}$-6(*S*)-Cyclo-5-diazouridine. Elimination of a Ring Carbonyl Group in Preference to Diatomic Nitrogen

Sir:

We wish to report an unusual reaction observed in connection with our studies on the thermal stability of certain 5-diazouracils.[1] We have now established that $O^{5'}$-6(*S*)-cyclo-5-diazouridine[1] (I) undergoes a novel ring contraction which proceeds with the loss of a ring carbonyl group in preference to diatomic nitrogen.

A solution of I (1.30 g) in acetonitrile[2] (200 ml) was heated in a steel reaction vessel at 100° for 18 hr and the solution then allowed to stand at ambient temperature for 18 hr to afford a white solid (II). Initial data indicated that I had been converted to uridine *via* a simple nitrogen elimination, since there was observed an absence of any absorption bands in the 2150-cm^{-1} region of the ir spectrum and specific peaks [B + H (112), B + 2H (113), S (133), M − 30 (214)] in the low resolution mass spectra were identical with those reported for uridine.[3] However, the uv spectrum of II revealed the absence of any absorption in the 230–346-nm region instead of the absorption maximum at 261 nm which is observed for uridine. Elemental analyses (C, H, N) were obtained for II and found to be consistent with the empirical formula $C_8H_{12}N_4O_5$[4] which definitely eliminated the possibility that II was uridine and established that carbon monoxide had been lost in preference to diatomic nitrogen. The structure of II was established on the basis of the following data.

The pmr spectra (DMSO-d_6, DMSO-d_6–D_2O) of II revealed a pattern of peaks in the δ 3.5–6.5 region which were indicative of a ribofuranosyl moiety. The presence of D-ribose was subsequently confirmed by treatment of II with dilute acid followed by a direct paper chromatographic comparison of the hydrolysate with authentic D-ribose and D-arabinose. This facile hydrolysis suggested that the ribosyl moiety was still bonded to a ring nitrogen. The pmr spectra of II also revealed the presence of two broad, exchangeable singlets (δ 7.75 and 7.50) which were suggestive of an amide group. Corroboration for the presence of a carboxamido group was provided when II gave a posi-

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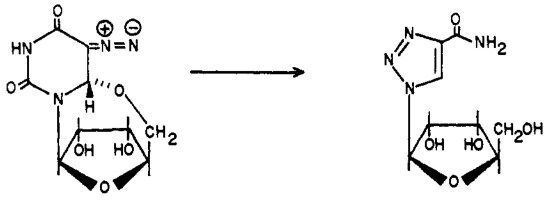
[1] T. C. Thurber and L. B. Townsend, *J. Heterocycl. Chem.*, **9**, 629 (1972).

[2] Mallinckrodt Chemical Works, St. Louis, Mo., Nanograde.

[3] K. Biemann and J. A. McCloskey, *J. Amer. Chem. Soc.*, **84**, 2005 (1962).

[4] The yield of purified material corresponding to this empirical formula was 78%.

tive hydroxylamine–ferric chloride test.[5] There remained one unassigned absorption peak in the pmr spectra which was assumed to be an aromatic ring proton on the basis of its chemical shift (δ 8.80, s, 1 H). These data were consistent with a disubstituted, five-membered heterocycle with three ring nitrogens (triazole). The formation of a triazole ring could occur by loss of the carbonyl group in the C-2 position of I followed by annulation between N-1 and the diazo group. If ring opening and rearrangement had occurred in the proposed manner then the structure for II must be 1-(β-D-ribofuranosyl)-1,2,3-triazole-4-carboxamide. The synthesis of this nucleoside had been previously reported[6,7] and a rigorous comparison with an authentic sample prepared by the procedure in ref 6 established that the compounds were identical in every respect.[8]



I II

We have established that the reaction of I proceeds with the loss of a ring carbonyl group in preference to diatomic nitrogen and to the best of our knowledge a reaction of this type has not been previously reported in the literature. The mechanism of this reaction is under active investigation in our laboratory using isotopes and derivatives which are closely related to I.

The ring contraction of I represents a convenient route to triazole nucleosides having other carbohydrate moieties[9] which would be accessible only under difficult isolation procedures from complex reaction mixtures; *e.g.*, a report has recently appeared[7a] describing the isolation of three isomeric triazole ribosides from an acid-catalyzed fusion reaction. It is of interest that the same type of acid-catalyzed fusion reaction using a 2-deoxyribose derivative[9] would be expected to give six different triazole nucleosides.

Acknowledgment. The authors wish to thank Dr. J. A. McCloskey for the mass spectral data reported in this communication. This investigation was supported by Public Health Service Research Grant No. CA 11147-04 from the National Cancer Institute.

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(5) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1964, p 137.

(6) G. Alonso, M. T. Garcia-Lopez, G. Garcia-Muñoz, R. Madroñero, and M. Rico, *J. Heterocycl. Chem.*, 7, 1269 (1970).

(7) (a) F. A. Lehmkuhl, J. T. Witkowski, and R. K. Robins, *J. Heterocycl. Chem.*, 9, 1195 (1972); (b) O. Makabe, S. Fukatsu, and S. Umezawa, *Bull. Chem. Soc. Jap.*, **45**, 2577 (1972).

(8) The following comparisons were made: melting point, mixture melting point, tlc, α, ir, uv, pmr, and mass spectra (both CI and EI).

(9) Evidence for the general nature of this rearrangement with respect to the carbohydrate moiety was obtained when $O^{5'}$-6(*S*)-cyclo-5-diazo-2′-deoxyuridine[1] was converted to a compound whose spectral data and empirical formula are consistent with the structure 1-(2-deoxy-β-D-ribofuranosyl)-1,2,3-triazole-4-carboxamide.

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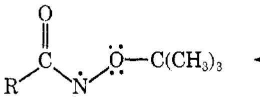
Additions and Corrections

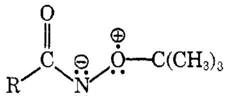
Thermal Decomposition of *N*-Nitrosohydroxylamines. V. Denitrosation and *N-tert*-Butoxyamido Radicals [*J. Amer. Chem. Soc.*, **94**, 2514 (1972)]. By T. Koenig,* J. A. Hoobler, and W. R. Mabey, Department of Chemistry, University of Oregon, Eugene, Oregon 97403.

Structures **8a**, **8b**, and **9** (below) did not appear in the original publication.

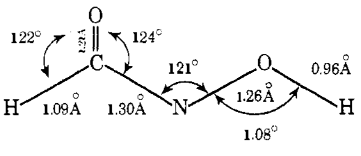
Also, Professor Danen has informed us that the esr spectrum referred to in footnote 8 was that of ethyl (*N-tert*-butoxy)carbamido radical rather than the propionamido species mentioned.



8a



8b



9

Radiation Chemistry of Nucleic Acids. Isolation and Characterization of Thymine Glycols [*J. Amer. Chem. Soc.*, **94**, 4764 (1972)]. By Bo-Sup Hahn and Shih Yi Wang,* Department of Biochemistry, School of Hygiene and Public Health, The Johns Hopkins University, Baltimore, Maryland 21205.

The nmr spectra were carried out with an external standard rather than an internal standard. For internal standards the δ values should be corrected to read: The trans isomer (I) has peaks for CH_3 (s, δ 1.28), C(6)H (d, δ 4.38, $J = 2.0$ Hz), C(5)OH (s, δ 5.73), C(6)OH (m, δ 6.28), N(1)H (d, δ 8.00, $J = 2.0$ Hz), and N(3)H (s, δ 9.33) in the nmr spectrum [in $(CD_3)_2SO$ at 100 MHz with internal standard $(CH_3)_4Si$]. Compound III has peaks for CH_3 (s, δ 1.28), C(6)H (s, δ 7.25), C(5)OH (br, δ 6.86), and N(3)H (br, δ 9.28) in the nmr spectrum.

The Use of Proton and Carbon-13 Nuclear Magnetic Resonance for Assignment of the Glycosylation Site in