

nitroamide II_d gave $k_e/k_\alpha = 6$. These data highlight the dependence of the stereochemistry of the reaction on the acid-base strength relationships, which relate to the rate of the proton capture by the carbanion.

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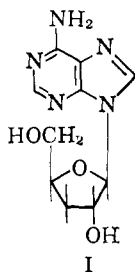
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3'-Deoxynucleosides. I. A Synthesis of 3'-Deoxyadenosine

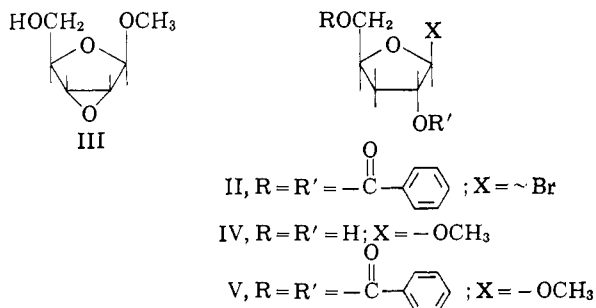
Sir:

The identity of cordycepin with 3'-deoxyadenosine (I) has recently been reported.¹ 3'-Deoxyadenosine has been shown to inhibit the growth of KB cell cul-



tures,² *B. subtilis*,³ an avian tubercle bacillus,³ and Ehrlich ascites carcinoma⁴ in mice, but its effects on other animal tumor systems have not yet been reported. In contrast to the large amount of work, both chemical and biological, carried out on 2'-deoxynucleosides, of the 3'-deoxynucleosides only 3'-deoxyadenosine^{5,6} and 3'-deoxyuridine⁷ appear to have been reported. Consequently, even though 3'-deoxyadenosine has been synthesized^{5,6} previously, we are now reporting its synthesis by a route providing a 3-deoxyribose derivative useful for synthesis of large amounts of 3'-deoxyadenosine, as well as being amenable to synthesis of 3'-deoxyadenosine-8-C¹⁴ and other 3'-deoxynucleosides.

For synthesis of 3'-deoxynucleosides, 2,5-di-*O*-benzoyl-3-deoxy- β -D-ribofuranosyl bromide (II) was chosen as a generally useful intermediate. Preparation of



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(4) D. V. Jagger, N. M. Kredich, and A. J. Guarino, *Cancer Res.*, **21**, 216 (1961).

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this new 3-deoxyribose derivative utilized methyl 2,3-anhydro- β -D-ribofuranoside (III)⁸ as the starting material. Stereospecific reduction of the epoxide function in III by hydrogenation in ethanol over a Raney nickel catalyst at 80° and 40 p.s.i.g. gave almost exclusively the 3-deoxyribose derivative, methyl 3-deoxy- β -D-ribofuranoside (IV), characterized by its infrared spectrum [2.92 (OH), 3.52 (OCH₃), no band at 11.6 μ (epoxide)] and n.m.r. spectrum [60 Mc., in CDCl₃, using a Varian Associates Model 4300B spectrometer: *O*-methyl protons, τ 6.16; C-1 proton, τ 5.22 (singlet)]. Benzoylation of IV with benzoyl chloride and pyridine gave methyl 2,5-di-*O*-benzoyl-3-deoxy- β -D-ribofuranoside (V), m.p. 80–81°, characterized by infrared and n.m.r. spectra and elemental analysis. Direct conversion of this methyl glycoside (V) to 2,5-di-*O*-benzoyl-3-deoxy- β -D-ribofuranosyl bromide (II) was accomplished by reaction with ten parts of a 16% solution of hydrogen bromide in acetic acid at 25° for 20 min. After removal of the solvents, II was obtained as an oil. Its n.m.r. spectrum no longer showed a band characteristic of the methoxyl function and the C-1 proton band was shifted downfield to τ 3.43.

The bromo sugar II was coupled with chloromercuri-6-benzamidopurine⁹ in refluxing xylene (15 min.) to give 6-benzamido-9-(2,5-di-*O*-benzoyl-3-deoxy- β -D-ribofuranosyl)purine, which on treatment with sodium methoxide in methanol gave 3'-deoxyadenosine (I), m.p. 224–225°; its infrared spectrum in Nujol was identical with that of an authentic sample.

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(9) C. D. Anderson, L. Goodman, and B. R. Baker, *ibid.*, **81**, 3967 (1959).

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Specific Reaction Rate of the Second-Order Formation of Ar₂⁺

Sir:

The formation of Ar₂⁺ by a bimolecular reaction involving an excited argon atom was first reported by Hornbeck and Molnar.¹ More recently, Fuchs and Kaul² and Dahler, Franklin, Munson, and Field³ reported kinetic studies of this second-order reaction. In neither of these latter mass spectrometric studies^{2,3} (which employed continuous electron beams and ion-repeller fields) could the specific reaction rate be determined explicitly because the reaction time, τ , was not known; the product of specific reaction rate and reaction time, $k\tau$, was reported. Combination of $k\tau$ values with the usual 10⁻⁸ sec. radiative lifetime leads to astonishingly high rate constants.³ Recently, Kaul⁴ has reported that three excited states of argon, with an

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(3) J. S. Dahler, J. L. Franklin, M. S. B. Munson, and F. H. Field, *J. Chem. Phys.*, **36**, 332 (1962).

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