nitroamide IId 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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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-

I
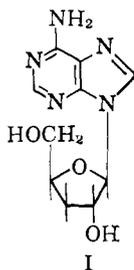
tures,[2] *B. subtilis*,[3] an avian tubercle bacillus,[3] and Ehrlich ascites carcinoma[4] in mice, but its effects on other animal tumor systems have not yet been reported. In contrast to the large amount of work, both chemical and biological, carried out on 2'-deoxynucleosides, of the 3'-deoxynucleosides only 3'-deoxyadenosine[5,6] and 3'-deoxyuridine[7] 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-C[14] and other 3'-deoxynucleosides.

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

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-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-benzamidopurine[9] 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.

Acknowledgment.—We are indebted to Dr. Nelson R. Trenner and Mr. Byron Arison for the n.m.r. spectra and their interpretation.

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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 Kaul[2] and Dahler, Franklin, Munson, and Field[3] 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, Kaul[4] has reported that three excited states of argon, with an

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effective lifetime of 1.1×10^{-6} sec., are involved in Ar_2^+ formation. Combination of this value with the results of Dahler, et al.,[3] yields a rate constant for Ar_2^+ formation of 3.2×10^{-10} cm.[3] molecule[-1] sec.[-1].

The pulse method of determining thermal rate constants of ion–molecule reactions, described by Tal'roze and Frankevich,[5] seems to afford an opportunity to obtain k and τ separately and has been applied in this laboratory to the second-order formation of Ar_2^+. In this method a pulsed electron beam is followed after a variable delay time by a pulsed ion-extraction field. Thus, with a large extraction field, the reaction time may be taken as the delay time plus any reaction time during the finite electron pulse.

For application to the second-order Ar_2^+ formation, consider the mechanism of Dahler, et al.,[3] viz.

$$Ar + e \xrightarrow{k_i} Ar^+ + 2e$$

$$Ar + e \xrightarrow{k_e} Ar^* + e$$

$$Ar^* + Ar \xrightarrow{k_r} Ar_2^+ + e$$

$$Ar^* + Ar \xrightarrow{k_u} Ar + h\nu$$
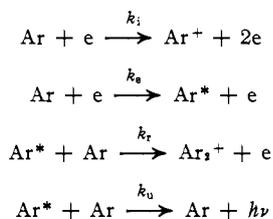
From this mechanism and the relationship

$$[Ar^*]_{t=0} = \left(\frac{k_e}{k_i}\right)[Ar^+]$$

it is easily shown that

$$\frac{[Ar_2^+]}{[Ar^+]} = \frac{\left(\frac{k_e}{k_i}\right)k_r[Ar]}{k_u + k_r[Ar]}\left\{1 - e^{-(k_u + k_r[Ar])(t_d + t_o)}\right\}$$

(1)

where t_d is the delay time and t_o is the reaction time during the electron pulse.

Measurements of $[Ar_2^+]/[Ar^+]$ (assuming it may be equated to the ion-current ratio I_{80}/I_{40}) have been carried out as a function of delay time, t_d, in a Bendix 14-101 time-of-flight mass spectrometer which has been modified by incorporating a closed ion source and differential pumping. The ion source was calibrated for gas concentration using the known rate of formation of CH_5^+ in methane.[5] Mass-dependent diminution of the ion beam occurs with increasing delay time so that it was necessary to construct discrimination curves at the pertinent masses and to correct all ion currents for this intensity decrease. In all experiments the nominal electron beam energy was that of the maximum in the Ar_2^+ ionization efficiency curve. At this electron energy, Dahler, et al.,[3] found $(k_e/k_i) = 0.055$.

The results for three pressures of argon are shown in Fig. 1. Here it can be seen that the general shape predicted by eq. 1 is obtained and that, moreover, the curves extrapolate to the time axis at a time that corresponds to $t_o = 0.12 \pm 0.02$ μsec. This is quite consistent with our measured pulse width and rise time of 0.25 and 0.11 μsec., respectively.

From best fits of the data, according to eq. 1, for the two higher pressures and the value[3] of 0.055 for k_e/k_i we find $k_r = 4.3 \pm 0.3 \times 10^{-10}$ cm.[3] molecule[-1] sec.[-1] and $k_u = 1/\tau_u = 2.1 \pm 0.2 \times 10^6$ sec.[-1]. The lowest pres-

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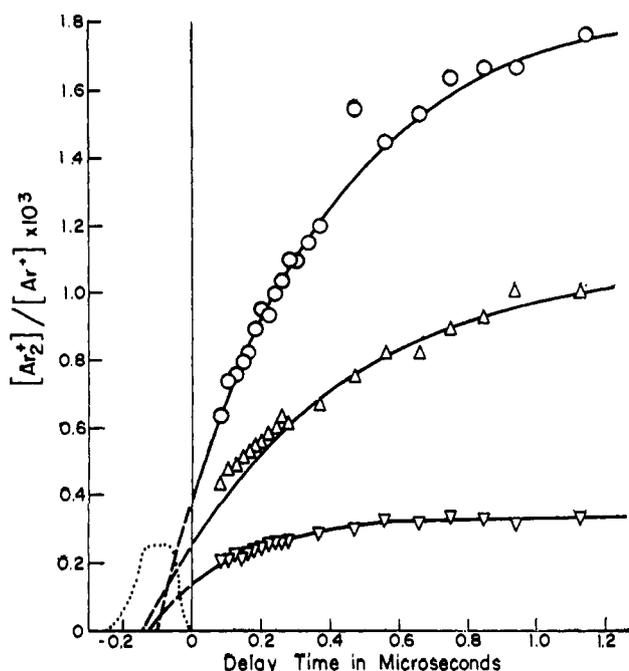
Fig. 1.—Dependence of ion-current ratio on delay time. Ar source pressures (microns): O, 5.2; Δ, 3.0; Δ, 1.0; . . . . ., electron beam pulse.

sure was not used in the determination of rate constants since reaction is nearly over even at the shortest delay times used.

The value of $k_r\tau_u$ from our work is 2.1×10^{-16} cm.[3] molecule[-1] which is to be compared with 3.6×10^{-16} found by Dahler, et al.[3] Considering uncertainties in the source concentrations and the diversity of the experiments, the agreement is satisfactory. Our value for τ_u of 4.8×10^{-7} sec. is in satisfactory agreement with the work of Kaul.[4] The value found for k_r corresponds to a cross section of the same order of magnitude as those of ordinary gas collisions.

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Correlation of Nuclear Spin Resonance Line Widths with Formation Constants of Weak Complexes

Sir:

In 1960, Jardetzky and Wertz[1] reported an observed broadening of the nuclear spin resonance absorption line of Na^{23} in the presence of certain anions and attributed this effect to an interaction of the Na^{23} nuclear quadrupole with an electric-field gradient caused by the formation of weak complexes of sodium with the added anions. Unfortunately, owing to the lack of independent data concerning such weak complexes, this interesting hypothesis could not be experimentally confirmed or examined for quantitative utility at that time.

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