Reduction of 1,2-Dichloro-1,2-di-(*p*-tolylsulfonyl)-ethene.[19]—A mixture of 0.65 g. (0.0016 mole) of 1,2-dichloro-1,2-di-(*p*-tolylmercapto)-ethene, 5.0 g. of zinc dust and 45 ml. of glacial acetic acid was stirred at reflux for 5 hours, and filtered while hot. The zinc residue was extracted with hot benzene and combined with the original filtrate before evaporating to dryness. The residues were combined, washed with water, filtered and dried to give 0.34 g. (63%) of crude product. This did not depress the melting point of an authentic sample of bis-(*p*-tolylsulfonyl)-ethene, m.p. 204–205°,[20] after one recrystallization from ethanol.

(19) This and the preceding experiment were performed by R. J. McManimie.

Acknowledgment.—The authors gratefully acknowledge support of this work by the Office of Ordnance Research, Department of the Army, under Contract No. DA-33-008-ORD 983.

(20) E. Fromm and E. Seibert, *Ber.*, **55B**, 1014 (1922).

LAFAYETTE, IND.

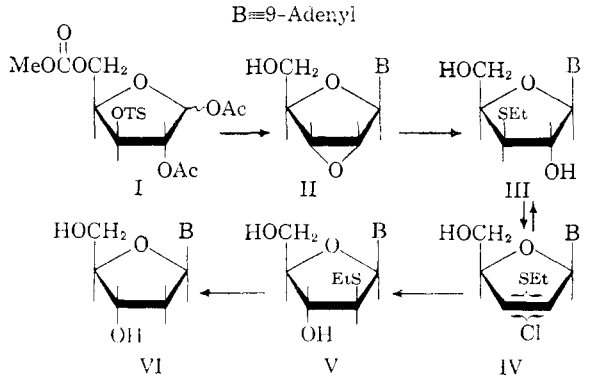
COMMUNICATIONS TO THE EDITOR

POTENTIAL ANTICANCER AGENTS.[1] SYNTHESIS OF 2′-DEOXYADENOSINE

Sir:

The first syntheses of pyrimidine 2′-deoxyribonucleosides have been announced within the past year.[2,3] This Communication reports the first synthesis of a purine 2′-deoxyribonucleoside, 2′-deoxyadenosine (VI). The method employed is independent of the nature of the substituent at C.1′ in contrast to the earlier pyrimidine 2′-deoxyribonucleoside syntheses, all of which involve participation of a 2-oxo- or 2-thiopyrimidine moiety.

1,2 - Di - *O* - acetyl - 5 - *O* - (methoxycarbonyl)-3-*O*-tosyl-D-xylofuranose[4] (I) was converted to the corresponding chloro sugar by treatment with ethereal hydrogen chloride and coupled with chloromercuri-6-benzamidopurine. The crude blocked nucleoside was converted to 6-amino-9-(2′,3′-anhydro-β-D-ribofuranosyl)-purine (II) [8.9% yield over-all from I; m.p. 200–203° dec.; $[\alpha]^{25}D$ −3° (0.6%[5]); C, 48.2; H, 4.72; N, 28.0][6] by treatment with methanolic sodium methoxide. Reaction of II with refluxing methanolic ethylmercaptide gave, as expected by analogy with methyl 2,3-anhydro-β-D-ribofuranoside,[7] predominantly 6-amino-9-(3′-deoxy-3′-ethylthio-β-D-xylofuranosyl)-purine (III) [66% yield (or 6.8% over-all from I without isolation of II); m.p. 135–155° and 181–182°; $[\alpha]^{27}D$ −76° (0.8%); C, 46.2; H, 5.77; N, 22.2; S, 10.0].



The isomer 6-amino-9-(2′-deoxy-2′-ethylthio-β-D-arabinofuranosyl)-purine (V) was obtained by a two-step procedure utilizing the powerful anchimeric effect of a neighboring sulfide group: (a) conversion of III to 6-amino-9-[3′(2′)-chloro-2′,-3′ - dideoxy - 2′(3′) - ethylthio - β - D - arabino-(xylo)furanosyl]purine (IV) [86% yield; m.p. 188–192° dec.; $[\alpha]^{26}D$ −60° (1.0% in chloroform); C, 43.2; H, 4.97; Cl, 10.9, 10.8; S, 9.74] by treatment with thionyl chloride at room temperature and (b) hydrolysis of IV with sodium acetate in refluxing 95% aqueous methyl Cellosolve. This afforded a mixture of III and V from which V [m.p. 211–213°; $[\alpha]^{25}D$ −65° (0.9%); C, 46.3; H, 5.12; N, 22.4; S, 10.6] could be separated in 58% yield.[8] Desulfurization of the triacetate of V with Raney nickel and deacetylation gave a 13% yield (based on unrecovered V) of synthetic 2′-deoxyadenosine (VI) [m.p. 184–186°; $[\alpha]^{23}D$ −25° (1.2% in water)]. Its identity with natural 2′-deoxyadenosine[9] was established by determination of the mixed m.p. (183–186°) and by the complete coincidence of the paper chromatographic behavior (in four solvent systems), X-ray diffraction patterns, and infrared and ultraviolet spectra of the two samples.

The preparation of two classes of fraudulent 2′-deoxyribonucleosides that may be of interest as antimetabolites should be possible. Use of this sequence with unnatural bases can give one class. Reaction of IV (where B = a natural base) with nucleophiles other than hydroxide ion could afford a second class of deoxynucleosides with a fraudulent 2′-deoxyribose moiety.

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(1) This work was carried out under the auspices of the Cancer Chemotherapy National Service Center of the National Cancer Institute, Contract No. SA-43-ph-1892.

(2) D. M. Brown, D. B. Parihar, C. B. Reese and A. Todd, *Proc. Chem. Soc.*, 321 (1957); *J. Chem. Soc.*, 3035 (1958).

(3) G. Shaw and R. N. Warrener, *Proc. Chem. Soc.*, 81 (1958).

(4) C. D. Anderson, L. Goodman and B. R. Baker, THIS JOURNAL, **80**, 5247 (1958).

(5) Unless otherwise stated, rotations were measured in 20% aqueous pyridine.

(6) The ultraviolet spectra of all the nucleosides described were compatible with their designation as 9-substituted adenines.

(7) C. D. Anderson, L. Goodman and B. R. Baker, THIS JOURNAL, **81**, in press (1959).

(8) Analogous reactions had first been studied on the corresponding methyl furanosides, see reference 7.

(9) The sample employed (m.p. 183–186°) was obtained from the California Corporation for Biochemical Research, Los Angeles 63, California.