indications that the procedure will permit the synthesis of boranes containing certain functional groups not compatible with the Grignard reagent. We are continuing to explore the synthesis of these substances.

This investigation was assisted by grants from The Upjohn Company, Parke-Davis and Company, and Merck and Company.

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6-FURFURYLAMINO-9-β-D-RIBOFURANOSYLPURINE: SYNTHESIS AND DIFFERENTIAL TOXICITY TO MAMMALIAN CELLS *IN VITRO*[1]

Sir:

The report[2,3] that 6-furfurylaminopurine (kinetin) stimulated division of certain plant cells in tissue culture prompted the preparation of 6-furfurylamino-9-β-D-ribofuranosylpurine (I) for inclusion in a current study[4] of the effects of 6-substituted glycosyl purines on normal and neoplastic mammalian cells.

Condensation of the chloromercuri derivative of 6-methylmercaptopurine[5] with 2,3,5-tri-O-acetyl-D-ribosyl chloride followed by deacetylation gave 43% of purified 6-methylmercapto-9-β-D-ribofuranosylpurine (II). The position and configuration of the glycosyl substituent in II was established by dethiolation with Raney nickel, from which 9-β-D-ribofuranosylpurine[6] was isolated in 65% yield. Reaction of II with furfurylamine, using the method of Hitchings, *et al.*,[5] for the synthesis of amino substituted adenines, gave I, m.p. 151–152° (from methanol), in 60% yield; λ_{max}^{EtOH} 267 mμ, ε = 19,300; R_f 0.72 and 0.89 in *n*-butanol–water and *n*-butanol–water–acetic acid (5:3:2), respectively, (calcd. for $C_{15}H_{17}N_5O_5$: C, 51.89; H, 4.93; N, 20.16. Found[7]: C, 51.48; H, 5.05; N, 20.23).

Dr. J. Brug[8] kindly supplied a sample of a riboside (III) obtained by reaction of the chloromercuri derivative of 6-N-acetyl-furfurylaminopurine with 2,3,5-tri-O-benzoyl-D-ribosyl chloride. The m.ps. (alone or admixed), ultraviolet spectra, and paper chromatographic behavior of I and III were identical.

I exhibits an unusual differential toxicity toward fibroblasts *in vitro*.[4] In semi-synthetic medium,[9] a 1×10^{-5} *M* solution killed 99% of the cells of a strain of adult human fibroblasts in 24 hours but was almost without effect on the rate of cell division or proportion of dead cells in three strains (HeLa, H.Ep.#1 and H.Ep.#2) of human carcinoma cells. Similarly, fibroblasts of embryonic mouse skin, growing in a medium of embryo extract and serum, are more severely damaged by a 1×10^{-5} *M* solution of I than are embryonic epithelial cells or cells of mouse sarcoma 180. Studies of the usefulness of I for ridding human cancer biopsy cultures of connective tissue cells are in progress.

THE SLOAN-KETTERING DIVISION OF CORNELL UNIVERSITY MEDICAL COLLEGE NEW YORK 21, N. Y. — ALEXANDER HAMPTON, JOHN J. BIESELE, ALICE E. MOORE, GEORGE BOSWORTH BROWN

RECEIVED AUGUST 31, 1956

THE STEREOCHEMICAL CONTROL OF LEAD TETRAACETATE AND TETRABENZOATE OXIDATIONS OF CYCLOPENTADIENE

Sir:

R. Criegee,[1] some years ago, oxidized conjugated dienes with lead tetracarboxylates obtaining esters of *cis* and *trans*-glycols[2] in low yield and since then the reaction has seen only limited use.[3] Further, it has resisted interpretation. This communication establishes its ionic nature[4,5] and describes its control.

The interesting isolation,[1a] in a single instance, of a monoester (3%) of *cis*-3,4-cyclopentenediol which indicated an hydroxyl source led us to the reaction of cyclopentadiene[6] (CPD) (1.5 equivalents) and lead tetraacetate (1.0 equivalents) in glacial acetic acid containing water[4] (1.5 equivalents) at 10–20° for one half hour. There was obtained each time a mixture of monoacetates in *75–80% yield*, once distilled, b.p. 108–110° at 12 mm., $n^{25}D$ 1.123 (*Anal.* Calcd. for $C_7H_{10}O_3$: C, 59.12; H, 7.10. Found: C, 59.10; H, 6.92). Catalytic hydrogenation[1a] yielded saturated monoacetates which on *p*-nitrobenzoylation gave *cis*-1-acetoxy-2-*p*-nitrobenzoxycyclopentane in excellent yield, m.p. 96–98°, reported[7] m.p. 96–97° (*Anal.* Calcd. for $C_{14}H_{15}O_6N$: C, 57.33; H, 5.16; N, 4.78. Found: C, 57.53; H, 5.02; N, 4.79). Saponification of the saturated monoacetates and *p*-nitrobenzylation yielded *cis*-1,2-di-*p*-nitrobenzoxycyclopentane (I), m.p. 116–118°, authentic sample,[7] m.p. 116–118°, m.m.p. 116–118°. Cleavage with periodic acid indicated 93% *cis*-1,2-cyclopentanediol and yielded glutardialdehyde 2,4-dinitrophenylhydrazone (88%) m.p. 159–160°, authentic sample, m.p.

(1) This investigation was supported by funds from the American Cancer Society, Inc., the National Cancer Institute, National Institutes of Health, Public Health Service (Grant Nos. C-471, C-678(C8) and C-1355), the Atomic Energy Commission (Contract No. AT(30-1)-910), and the Damon Runyon Memorial Fund for Cancer Research.

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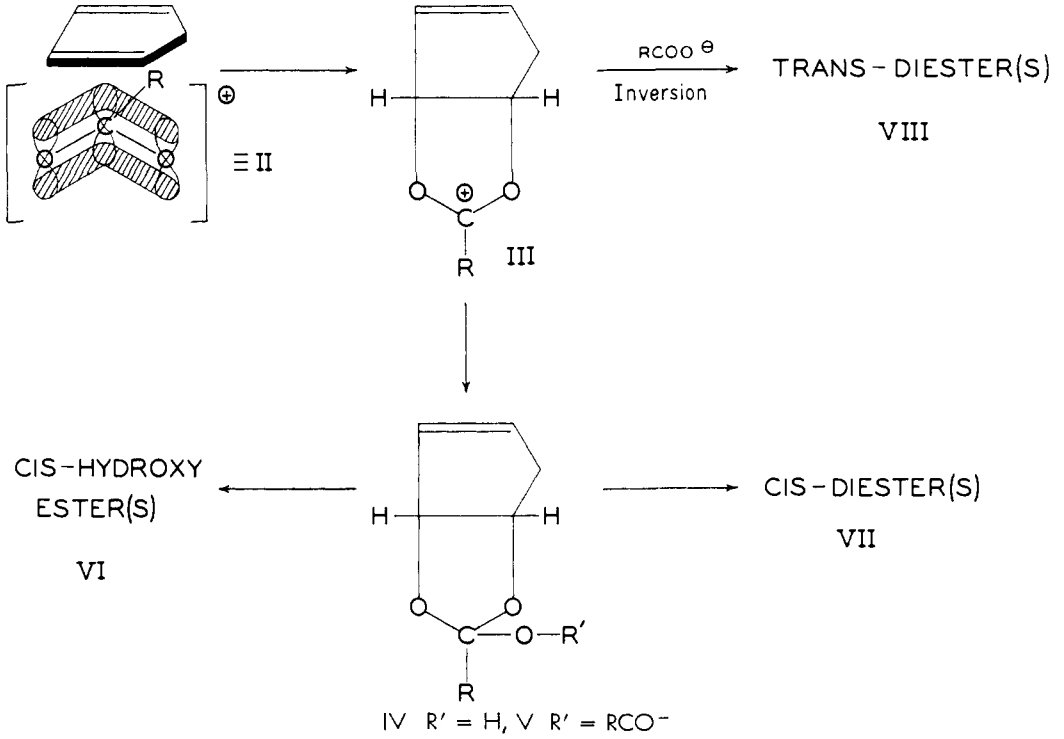

159–160°, m.m.p. 159–160°. *trans*-1,3-Cyclopentanediol[7b] also was obtained from the cleavage mixture as the di-*p*-nitrobenzoate, m.p. 184–185°, reported[7] m.p. 186° and the diurethan, m.p. 172–173°, reported[7] m.p. 173°. Oxidation in anhydrous acetic acid gave *cis* and *trans*-3,4-diacetoxycyclopentene (37%), proven as before.

Oxidation in dry acetic acid with one equivalent[4] of potassium acetate added gave 44% of a product shown later by periodic acid titration to be 97% *trans*-3,4-diacetoxycyclopentene, b.p. 85° at 1 mm. (*Anal.* Calcd. for $C_9H_{12}O_4$: C, 58.68; H, 6.57. Found: C, 58.85; H, 6.75), transformed similarly to *trans*-1,2-di-p-nitrobenzoxycyclopentane, m.p. 143–145°, m.m.p. 143–145°. In addition, a 3% yield of triester was obtained which was hydrolyzed to *trans*-3,4-cyclopentenediol and potassium glycolate.[1a]

Reaction of lead tetrabenzoate and CPD[1a]: in wet benzene gave a sufficient amount of benzoic acid and a non-crystalline *cis*-hydroxybenzoate (41%) transformed similarly to give *cis*-1-benzoxy-2-*p*-nitrobenzoxycyclopentane (64%), m.p. 88–89° (*Anal.* Calcd. for $C_{19}H_{17}O_6N$: C, 64.23; H, 4.82; N, 3.94. Found: C, 64.13; H, 4.63; N, 3.91) and to give I, m.p. 116–118°, m.m.p. 116–118°.

In interpreting this, we invoke a Winstein neighboring cation,[4] III, which opens *cis* with water (III → IV → VI) or carboxylic solvent (III → V → VII) and *trans* with carboxylate anion (III → VIII) utilizing the reactivity sequence, $H_2O > RCO_2^{\ominus} > RCO_2H$.

In Criegee's experiments,[1] the stereochemistry of the 1,2-products was controlled by traces of water until consumed (III → IV → VI), then by carboxylic solvent (III → V → VII) until the effective anion concentration from divalent lead salts became dominant (III → VIII).

Utilizing Mosher's postulate,[5] $RCO_2^{\oplus}$ (II) or its equivalent, we account for the formation of III by attack[8] of II on CPD and for glycolic ester formation by attack on the α-position of the diesters. Evidence of free radical attack was not found.[1d,9]

An Armstrong Cork Co. Fellowship (F. J. V.) and a du Pont Co. Summer Faculty Fellowship (F.V.B., Jr.) are gratefully acknowledged.

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METHYL AFFINITIES OF ETHYLENE, TETRAFLUOROETHYLENE AND TETRACHLOROETHYLENE[1]

Sir:

In the course of our studies of methyl affinities of aromatic and olefinic compounds we determined the relative rates of addition of methyl radicals to ethylene, tetrafluoroethylene and tetrachloroethylene. The results obtained demonstrate some fundamental principles governing the rate of radical addition reactions thereby deserving further discussion.

The methyl affinities are determined by a method described elsewhere,[2,3,4] and represent the ratio k_2/k_1.

(1) This work was supported by a grant from the National Science Foundation.

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