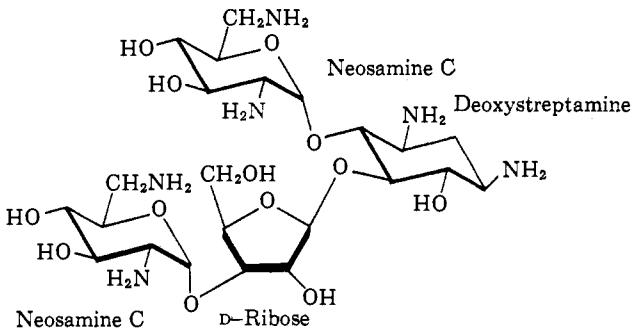
From this assignment, it follows directly that the absolute stereochemistry of deoxystreptamine in neamine is as shown in Ie. The neamine component of neomycins B and C is identical and substituted deoxystreptamine structures If and Ig may be written for the antibiotics themselves. Since Ib is also obtained from poly-O-methyl-penta-N-acetylparomomycin,[3a] and from the poly-O-methyl-N-acetyl derivatives of zygomycins A_1 and A_2[3b] (probably identical with paromomycins I and II), the substituted deoxystreptamines in these antibiotics are Ih for paromomycin–zygomycin A_1, and probably Ii for paromomycin II–zygomycin A_2. Moreover, the very recent isolation of paromamine[8] [Ij; 4-(2-amino-2-deoxy-α-D-glucosyl)-deoxystreptamine] from partial hydrolysis of kanamycin C[9] establishes the absolute configuration of deoxystreptamine in that antibiotic[10] as in Ik. Also, since kanamycins A[11] and B,[12] like kanamycin C,[10] contain kanosamine (3-amino-3-deoxy-D-glucose) and deoxystreptamine, but differ from kanamycin C in the replacement of its glucosamine fragment by 6-aminoglucose in kanamycin A and by an unidentified diaminohexose[13] (on biogenetic grounds this should be neosamine C) in kanamycin B, the absolute stereochemistry of deoxystreptamine in these antibiotics is almost certainly as in Il and Im, respectively.

With the assignment of this last stereochemical point the structure of neomycin C is completed and may be written as shown.



Neomycin C

Complete structures of neomycin B and paromomycin await further evidence for the stereochemistry of neosamine B. The cuprammonium method provides further evidence on this point, as well. As expected, a high positive increment is observed in the rotation of methyl N,N′-diacetyl-α-neosaminide C (a 2,6-diamino-D-glucose derivative, with free hydroxyl groups at C-3 and C-4) in cuprammonium B solution; $\Delta[M]_{\text{Cupra B}} = +2280°$. Of greater significance is the strong positive increment of methyl N,N′-diacetyl-α-neosaminide B; $\Delta[M]_{\text{Cupra B}} = +1880°$. Though this observation does not of itself exclude L-talose or L-altrose stereochemistry for neosamine B, it does exclude the five other isomers allowed by neosamine B's stereochemistry at C-2[14,15] (with the amino group on the right in the Fischer projection formula) and is most consistent with the previously suggested[2] 2,6-diamino-2,6-dideoxy-L-idose stereochemistry.

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1,1,1,4,4,4-HEXAFLUORO-2,3-DIPHENYL-2,3-BUTANEDIOL

Sir:

We wish to report the observation of a remarkable resistance to pinacol–pinacolone rearrangement exhibited by a symmetrical alkyl aryl ethanediol.

1,1,1,4,4,4-Hexafluoro-2,3-diphenyl-2,3-butanediol (I) was prepared in 17% yield by the photopinacolization reaction between 13 g. of trifluoromethyl phenyl ketone[1] and 75 ml. of 2-propanol in a quartz tube at 5 cm. from a Hanovia 16A-13 mercury vapor lamp. Distillation of the solvent and recrystallization of the residue from 80:20 hexane–ether produced 2.16 g. of white needles. These were further purified by sublimation *in vacuo;* m.p. 155–156°. (*Anal.* Calcd. for $C_{16}H_{12}O_2F_6$: C, 54.86; H, 3.45. Found: C, 55.10; H, 3.38.)

The compound possessed an infrared spectrum, in KBr disk, completely consistent with its assignment as the pinacol: −OH, 3440–3600 cm.$^{-1}$; −CF_3,[2] 1165–1210 cm.$^{-1}$; and the complete absence of carbonyl absorptions.

Oxidative cleavage of I with lead tetraacetate in boiling acetic acid gave only trifluoromethyl phenyl ketone, identified as its 2,4-dinitrophenylhydrazone: m.p. and mixture m.p. 108–109°; literature m.p. 106–107°.[3]

The pinacol was found to be completely resistant to several concentrations of sulfuric acid in acetic acid at steam bath temperatures. It could be recovered unchanged from 38% sulfuric acid after 4 hr. heating and from 65% sulfuric after 6 hr. heating. It resisted the action of boiling acetic acid-β-naphthalenesulfonic acid for 30 hr.

The non-fluorinated analog of I, 2,3-diphenyl-2,3-butanediol,[4] prepared by the addition of excess methyllithium to benzil, could be transformed into 3,3-diphenyl-2-butanone by much less vigorous conditions: 0.6% *p*-toluenesulfonic acid or 0.6% iodine in acetic acid after 0.5 hr. reflux.

The resistance of I to acidic conditions substantially in excess of those required to rearrange similar diols may be interpreted as a destabilizing influence of the powerfully electron attracting trifluoromethyl group to the development of carbonium character on the hydroxyl-bearing carbons. Such carbonium character is generally agreed to be a prerequisite to the rearrangement step.[5]

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(1) The ketone was synthesized according to the procedure of A. Sykes, J. C. Tatlow and C. R. Thomas, *Chem. Ind.* (London), 630 (1955).

(2) In agreement with previous spectral investigations of the −CF_3 group, an intense absorption band consisting of a series of multiple peaks is observed: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 330.

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