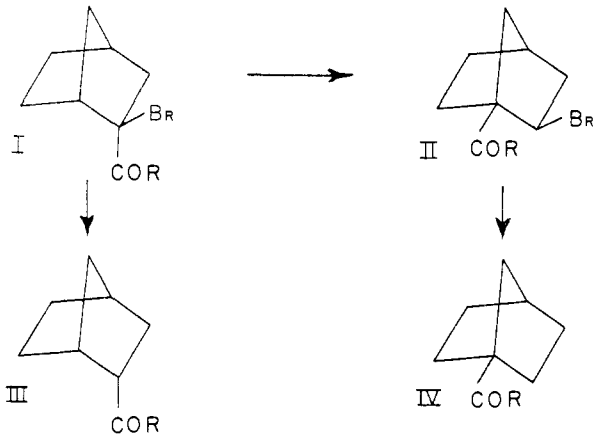
norbornane-1-carboxamide although the position and configuration of the bromine has not been proved.



2-*exo*-Bromonorbornane-2-*endo*-carbonyl chloride (I, R = Cl, b.p. 95–98° (7 mm.)) was prepared by brominating norbornane-2-*endo*-carbonyl chloride (III, R = Cl)[5] in boiling thionyl chloride. Treatment of the bromoacyl halide with anhydrous ammonia in cold ether gave 2-*exo*-bromonorbornane-2-*endo*-carboxamide (I, R = NH_2; m.p. 119.5–121° from toluene. Found: C, 44.34; H, 5.62; N, 6.26; Br, 36.30). Catalytic reduction with zinc and acetic acid[6] gave norbornane-2-*endo*-carboxamide (III, R = NH_2; m.p. 210–211°; reported[7] m.p. 205–206°).

When compound I (R = NH_2) was heated for three minutes at 150–160°, 76% of the isomeric carboxamide (II, R = NH_2; m.p. 173–174° from toluene. Found: C, 44.28, H, 5.62; N, 6.34; Br, 36.76) was obtained. Compound I (R = NH_2), in a solution of 2% potassium hydroxide in 95% methanol, was rearranged quantitatively to II (R = NH_2) in six hours at room temperature. The latter, upon catalytic hydrogenation (Pd-$CaCO_3$) or reduction with zinc and acetic acid,[6] gave norbornane-1-carboxamide (IV, R = NH_2; m.p. 234–236° from water), identified by mixed melting point and by comparison of the infrared spectrum with that of an authentic sample (m.p. 234–236°. Found: C, 68.75; H, 9.25; N, 9.92) prepared from norbornane-1-carboxylic acid (IV, R = OH).[2] Saponification of IV (R = NH_2), gave the free acid IV (R = OH; m.p. 111–112°; reported[2] m.p. 112–113°).

2-*exo*-Bromo-2-*endo*-carbomethoxynorbornane (I, R = OCH_3; b.p. 98–99° (5 mm.), $n^{24.5}D$ 1.5043. Found: C, 46.42; H, 5.36) was obtained from the acid chloride I (R = Cl) by treatment with methanol. Catalytic[8] or chemical[6] hydrogenolysis of this ester gave only 2-*endo*-carbomethoxynorbornane (III, R = OCH_3) which was identified by saponification to norbornane-2-*endo*carboxylic acid (III, R = OH; m.p. 65–66°, reported[5] m.p. 65–66°).

(5) K. Alder, G. Stein, M. Liebmann and E. Rolland, *Ann.*, **514**, 197 (1934).

(6) E. Ott and K. Krämer, *Ber.*, **68**, 1655 (1935).

(7) G. Komppa and S. Beckmann, *Ann. Acad. Sci. Fennicae*, **A39**, No. 7 (1934).

(8) L. F. Fieser and W. T. Huang, THIS JOURNAL, **75**, 4837 (1953).

Bromination[9] of III (R = OH), on the other hand, gave the rearranged bromoacid II (R = OH; m.p. 150–151° from toluene or heptane; (Found: C, 43.58; H, 5.31) which, upon treatment with diazomethane, gave the isomeric methyl ester II (R = OCH_3; b.p. 117–118° (5 mm.), $n^{24.5}D$ 1.5055. Found: C, 46.25; H, 5.72). Hydrogenolysis[7,8] of the latter and saponification of the resulting debrominated ester IV (R = OCH_3) gave IV (R = OH) as the sole product. The acid IV (R = OH) also was obtained by hydrogenolysis[8] of the bromoacid II (R = OH).

It therefore appears highly probable that the bromonorbornanecarboxylic acid and its methyl ester reported by Kwart and Null[1] were rearranged already prior to hydrogenolysis.

(9) Bromination was by the general method of C. S. Marvel in E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955 p. 523.

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RECEIVED JANUARY 23, 1958

KANAMYCIN. V. THE STRUCTURE OF KANOSAMINE

Sir:

Kanosamine,[1] the remaining unknown moiety of kanamycin,[2] has been shown[3] to be a straight chain 3-amino-3-deoxyaldohexopyranose, which from deamination studies could be either 3-amino-3-deoxy-D-allose or 3-amino-3-deoxy-D-glucose. N-Acetylkanosamine was refluxed in methanolic hydrogen chloride, acetylated (NaOAc, Ac_2O), and recrystallized (ethanol) to give methyl kanosaminide tetraacetate[4], $[\alpha]D$ +105.5° (*c* 0.5, $CHCl_3$), m.p. 172.5–173°. *Anal.* Calcd for $C_{15}H_{23}NO_9$: C, 49.9; H, 6.42; N, 3.88. Found: C, 50.1; H, 6.61; N, 3.78. This product was identical by infrared spectrum and mixed melting point comparison with methyl 3-amino-3-deoxy-α-D-glucopyranoside tetraacetate prepared according to Peat and Wiggins,[5] proving that kanosamine is 3-amino-3-deoxy-D-glucose (3-D-glucosamine). Kanosamine pentaacetate[1] was identical in infrared spectrum and melting point behavior with 3-β-D-glucosamine pentaacetate prepared from the synthetic methyl glycoside tetraacetate by hydrolysis and reacetylation.

The infrared spectrum in KBr pellet of kanamycin base showed bands at 838 and 823 $cm.^{-1}$, with similar bands present at 841 and 821 $cm.^{-1}$ in the spectrum of the sulfate, indicative of two alpha-glycosidic linkages in the kanamycin molecule.[6]

(1) M. J. Cron, O. B. Fardig, D. L. Johnson, H. Schmitz, D. F. Whitehead, I. R. Hooper and R. U. Lemieux, THIS JOURNAL, **80**, 2342 (1958).

(2) T. Takeuchi, T. Hikiji, K. Nitta, S. Yamazuki, S. Abe, H. Takayama and H. Umezawa, *J. Antibiotics*, Ser. A, **10**, 107 (1957); M. J. Cron, D. L. Johnson, F. M. Palermiti, Y. Perron, H. D. Taylor, D. F. Whitehead and I. R. Hooper, THIS JOURNAL, **80**, 752 (1958).

(3) M. J. Cron, O. B. Fardig, D. L. Johnson, D. F. Whitehead, I. R. Hooper and R. U. Lemieux, *ibid.*, **80**, 4115 (1958).

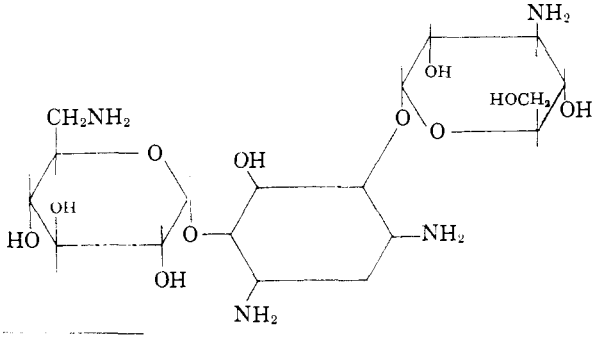
(4) K. Maeda, M. Murase, H. Mawatari and H. Umezawa, *J. Antibiotics*, **A11**, 73 (1958).

(5) S. Peat and L. F. Wiggins, *J. Chem. Soc.*, 1810 (**1938**).

(6) Barker, *et al.* [*J. Chem. Soc.*, 171 (1954); *Methods of Biochemical Analysis*, **3**, 213 (1956)] have considered the 844 ± 8 $cm.^{-1}$ region to be diagnostic of the α-glucopyranose structure. This region must be broadened as shown by the occurrence of bands at 827 $cm.^{-1}$ in melezitose and at 833 $cm.^{-1}$ in N-acetyl-3-α-D-glucosamine.

The strongly dextrorotatory properties of kanamycin, tetra-N-acetylkanamycin and especially kanamycin decaacetate[4], $[\alpha]^{24}D$ +117° (*c* 1, $CHCl_3$), support this configurational assignment. As expected, the rotation of acetylated derivatives of 3-D-glucosamine and 6-D-glucosamine[1] agree closely with the rotations of the corresponding glucose derivatives. The contribution of each of the two anomeric centers to the molar rotation (106,000) of kanamycin decaacetate must be in the order of +25,000 ± 5,000.[7] The remaining portions of each of the acetylated sugar residues may be assigned a contribution of about +20,000. Thus the total contribution of the two sugar residues, assuming the *alpha*-D configuration, must be in the order of 90,000 ± 10,000. The magnitudes of the molar rotations generally found for acetylated carbohydrates clearly favor a contribution of 16,000 ± 10,000 by the 2-deoxystreptamine moiety, compared to 66,000 or 116,000 which would be required if one or both of the glycosidic unions were of the *beta*-D-configuration.

These data allow one to write a structure for kanamycin, in which the only remaining problem is that of determining the order of attachment to the 4(6) and 6(4) positions on the all-*trans* 2-deoxystreptamine.



(7) C. S. Hudson, THIS JOURNAL, **31**, 66 (1909).

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RECEIVED JULY 9, 1958

NEW PRODUCTS FROM THE REACTION OF BENZOYL PEROXIDE WITH BENZENE[1]

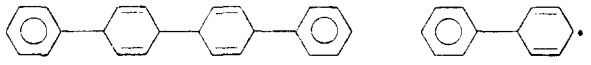
Sir:

We have been reinvestigating the reactions of aroyl peroxides with benzene at relatively high dilution in a study of the detailed reaction mechanisms. Previous product studies[2] have utilized quite concentrated solutions leading to results complicated by induced decomposition of the peroxide and by the attack of radicals on the initial products.

(1) This research was supported by the United States Air Force under Contract No. AF 49(638)-88 monitored by the AF Office of Scientific Research of the Air Research and Development Command.

(2) (a) *Cf. e.g.* the summary by C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 482; (b) B. M. Lynch and K. H. Pausacker, *Austral. J. Chem.*, **10**, 40 (1957).

We have discovered two significant new products of the thermal decomposition of benzoyl peroxide (20 g.) in benzene (4 l.) at reflux under nitrogen. In addition to the expected carbon dioxide (1.7 mole per mole of peroxide), benzoic acid (0.1 mole) and biphenyl (0.6 mole), we obtained a solid, m.p. 145–146°, identified as 1′,4′,1″,4″-tetrahydro-*p*-quaterphenyl (I) (0.03 mole) and a liquid (isolated by chromatography of the biphenyl fraction on alkaline Grade I alumina using hexane) identified as 1,4-dihydrobiphenyl (0.4 mole). We also have some evidence of 1,2-dihydrobiphenyl.



I II

The tetrahydroquaterphenyl (I) had C, 92.9; H, 7.18; mol. wt. (Signer), 303. Calcd. for $C_{24}H_{22}$: C, 92.86; H, 7.14; mol. wt. 310. It absorbed four moles of hydrogen to give the dodecahydroquaterphenyl, m.p. 202°; C, 90.0; H, 9.44. Calcd. for $C_{24}H_{30}$: C, 90.5; H, 9.50. On dehydrogenation at 300° over palladium on carbon *p*-quaterphenyl was formed, but some cleavage to biphenyl also occurred. The ultraviolet spectrum of the tetrahydroquaterphenyl is similar to that of toluene, indicating that the double bonds are not conjugated with each other nor with a benzene ring. The relatively high m.p. suggests that the compound is the nearly planar all-*cis* isomer.

1,4-Dihydrobiphenyl prepared by the Birch reduction of biphenyl[3] also has an ultraviolet curve similar to that of toluene. The infrared spectra of the initial oily fraction isolated by chromatography and the synthetic dihydrobiphenyl correspond exactly. However the ultraviolet spectra of the total dihydrobiphenyl fraction isolated by gas chromatography had an absorption maximum of 256 mμ with an apparent ε of 2000–3000, suggesting strongly the presence of some 15–30% of 1,2-dihydrobiphenyl.

Although the phenylcyclohexadienyl radical (II, and other contributing structures) is the most plausible of the previously suggested intermediates in biphenyl formation,[2] the present isolation of its combination and disproportionation products is the first direct experimental evidence for this key intermediate. We feel that this evidence taken with other data regarding radical reactivities effectively eliminates a different mechanism of biaryl formation suggested several years ago.[4]

The biaryl products obtained in a solvent such as nitrobenzene are now seen to depend on at least two distinguishable processes (a) the relative rates of formation of the isomeric substituted phenylcyclohexadienyl radicals and (b) the subsequent possibly differing rates of these radicals. It is therefore to be expected that precise values of the reactivity ratios will vary somewhat with the experimental conditions used although large variations are unlikely.[2a] Detailed interpretations of such ratios clearly require further careful studies of these systems.

(3) W. Hückel and E. Schwen, *Ber.*, **89**, 50 (1956).

(4) D. F. DeTar and S. V. Sagmanli, THIS JOURNAL, **72**, 965 (1950).