

(3H) and a broad peak (4H) assigned to the propyl side chain where IIIb has a triplet (3H) and a broad peak (2H) attributable to an ethyl side chain. The similarity of IIIa and IIIb in specific rotation $(-46.8^{\circ})^{\circ}$ and -46° , respectively) and n.m.r. spectra is suggestive of identical stereochemistry.¹



Crystalline U-11,921 hydrochloride (Ic), C19H36N2- $O_6S \cdot HC1 \cdot H_2O$, $[\alpha]^{25}D + 143^\circ$, contains one basic function, pK_a' 7.73, one NCH₃, and three $-C-CH_3$ groups. The n.m.r. spectra of Ic and Ia differ in that the sharp singlet at 125 c.p.s. (3H) attributable to the -SCH3 group present in Ia is missing in the spectrum of Ic. Instead, it shows a quadruplet at 147, 155, 162, and 170 c.p.s. and a triplet at 65, 75, and 85 c.p.s., assigned to an -SCH₂CH₃ group; *i.e.*, the structure of U-11,921 is represented by Ic. In addition, hydrazinolysis of Ic, followed by acid hydrolysis, afforded crystalline 4-*n*-propyl-L-hygric acid (IIIa). The remaining fragment was isolated as crystalline colorless base, $C_{10}H_{21}NO_5S$ (IIb), m.p. 191–195° dec., $[\alpha]^{25}D + 258^{\circ}$ $(c \ 0.7, \text{ water}), pK_a' \ 7.17, \text{ equiv. wt. } 271 \ (calcd. \ 267).$ The n.m.r. spectrum of IIb, called ethyl α -thiolincosaminide, differs from that of IIa in that the sharp singlet (3H), due to the -SCH₃ group present in IIa, has been replaced by a quadruplet at 150, 157, 164, and 171 c.p.s. and a triplet at 71, 78, and 85 c.p.s. which have been assigned to an -SCH₂CH₃ group. Thus, IIb has structure identical with that of IIa except for the substitution of the -SCH₃ group of IIa by an -SCH₂CH₃ in IIb.

Crystalline U-11,973 hydrochloride (Id), $C_{17}H_{32}$ -N₂O₆S·HCl·H₂O, $[\alpha]^{25}D$ +149° (c 0.9, water), contains one -SCH₃, two C-CH₃, and one basic function, pK_a' 7.58, equiv. wt. 445 (calcd. 446.5). Infrared absorptions at 1687 and 1596 cm.⁻¹ indicated an amide linkage. Due to the limited solubility of Id in desirable solvents, the n.m.r. spectrum had limited usefulness, but did indicate close similarity to the other lincomycin-related antibiotics, with the striking exception of the absence of the signal attributed to the $-NCH_3$ group. Methylation of Id with methyl iodide afforded lincomycin (Ia), identified by paper and thin layer chromatography, specific rotation, and infrared and n.m.r. spectra. Thus, the structure of U-11,973 is Id, N-demethyllincomycin.

Crystalline U-20,943 hydrochloride (Ie), $C_{18}H_{34}$ -N₂O₆S·HCl·H₂O, $[\alpha]^{25}D$ +153°, pK_a' 8.00, contains two C-CH₃, but no -SCH₈ or -NCH₃. That Ie could be the structure for U-20,943 was suspected because of its manner of preparation. This was proven by reacting U-20,943 with CH₃I and isolating U-11,921 (Ic), identified as such by paper and thin layer chromatography, rotation, and infrared and n.m.r. spectra.

Antibiotics U-11,973 and U-20,943 have been used as starting materials for a series of N-substituted analogs. This work will be the subject of a future communication.

We gratefully acknowledge the analytical and spectral work of Drs. W. A. Struck and G. Slomp and associates.

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Received October 3, 1964

Synthesis of a Novel Heterobicycloalkane Containing Boron and Phosphorus

Sir:

A recent review on heterocyclic organic boron compounds¹ has shown the absence of information on such compounds containing both boron and phosphorus. We would like to report the synthesis of such a compound, 1,5-diphenyl-1-bora-5-phosphabicyclo[3.3.0]octane (I). The compound, stable in the atmosphere,



was prepared in 28% yield by refluxing a dilute toluene solution containing equimolar quantities of triethylamine-phenylborane and diallylphenylphosphine. The triethylamine-phenylborane was synthesized by the method of Hawthorne² and the diallylphenylphosphine by the method of Jones, *et al.*³ The product was isolated by distilling the reaction mixture into crude fractions and crystallizing the product from acetone at low temperatures. Recrystallization yielded a white solid, m.p. 75.5-76.5°.

Anal. Caled. for $C_{18}H_{22}BP$: C, 77.16; H, 7.92; B, 3.86; P, 11.05; mol. wt., 280. Found: C, 77.08; H, 7.71; B, 4.02; P, 10.90; mol. wt., 287 (vapor pressure osmometer).

The infrared spectrum of the product showed no boron-hydrogen or olefinic bonds in accord with the assigned structure which results from intramolecular

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- (2) M. F. Hawthorne, J. Am. Chem. Soc., 80, 4291 (1958).
- (3) W. J. Jones, W. C. Davies, S. T. Bowden, C. Edwards, V. E. Davis. and L. H. Thomas, J. Chem. Soc., 1446 (1947).

hydroboration of the two olefinic bonds of diallylphenylphosphine by phenylborane. The n.m.r. spectrum was in complete agreement with the assigned structure. The boron resonance was recorded at +23p.p.m. relative to trimethyl borate as reference. The p.m.r. spectrum gave a peak area for aromatic protons of 10.0 and for aliphatic protons of 12.5. The aromatic protons gave a complex pattern of peaks bounded by τ 3.13 and 3.31 and centered at 3.2. The aliphatic protons gave a complex pattern with peaks centered at τ 8.39, 9.04, and 9.61. The spectrum was obtained from a carbon tetrachloride solution of the compound using acetaldehyde as the external standard. Unlike analogous diallylamines, only one product was isolated from this reaction.⁴ In the case of the nitrogen analogs, monocyclic 1,2-azaborolidines were also isolated, apparently having been formed by intramolecular reduction of an allylic carbon-nitrogen bond. The fact that the monocyclic product does not form in the phosphorus case suggests that the boron-phosphorus bond is not as stable as the boron-nitrogen bond. This is in accord with the dissociation energies for complexes of trimethylamine and trimethylphosphine with trimethylborane, which have been found to be 17.6 kcal./mole and 16.5 kcal./mole, respectively.5,6

The compound was found to be unusually thermally stable. Thermal gravimetric analysis of the compound revealed that it retained 95% of its original weight at 350° and 30% of its original weight at 500° .

Acknowledgments.—We are grateful to the National Lead Foundation for support of this research in the form of a fellowship. We are also grateful to Dr. Wallace S. Brey, Jr., of this department, for determination and interpretation of the n.m.r. spectra, and to Dr. P. E. Slade of Chemstrand Research Center for the thermal gravimetric analysis.

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(b) H. C. Brown, M. D. Taylor, and M. Gerstein, *ibid.*, 66, 431 (1944).
(6) H. C. Brown, J. Chem. Soc., 1248 (1956).

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Received September 14, 1964

Phenylated Dihydrofurans. Photo- and Acid-Catalyzed Rearrangements and Intermediacy in Cyclopropyl Ketone Cleavage¹

Sir:

This concerns novel photochemistry in a new area stemming from our recent investigation of the $5\rightarrow 2$ phenyl group migration during pyrolysis and photolysis of bis(2,3,5,5-tetraphenyl-2-dihydrofuranyl)hydrazine.² 2,3,5,5-Tetraphenyl-2,5-dihydrofuran (I^{2a}) was made and shown not to be involved in this rearrangement.^{2a} The dihydrofuran I and its 4,5-isomer II³ were selected for further study because the former (an allyl ether) could cleave at either C–O bond to

(3) See Analytical Data section.

give an acyclic unsaturated ketone (III or V), whereas the latter (an enol ether) would be expected to break at the 1,5 C–O bond with possible valence tautomerization to the cyclopropyl ketone IV.



The 2,5-dihydrofuran (I) upon irradiation^{2b} (10⁻³ M in benzene) underwent 1,2 ring cleavage at the presumably stronger C–O bond, with 5→4 phenyl group migration, and gave the acyclic β , γ -unsaturated ketone, 1,2,3,4-tetraphenyl-3-buten-1-one (III,³ 37%, structure shown by spectral data,³ n.m.r. spectrum of its carbinol, 1,2,3,4-tetraphenyl-3-buten-1-ol, and by ozonolysis to dibenzoylphenylmethane and benzalde-hyde). This apparently novel rearrangement may be classed as a vinylogous pinacol type in which the oxygen atom plays the dual role of the two hydroxyls of a pinacol.^{2a,4}

In contrast to photolysis the 2,5-dihydrofuran (I) under acid catalysis underwent cleavage at the presumably weaker 1,5 C–O bond, without phenyl group migration, and it gave the isomeric β , γ -unsaturated ketone V^{4a} (64%), presumably through the enol of V, possibly via the 4,5-dihydrofuran II.

2,3,5,5-Tetraphenyl-4,5-dihydrofuran (II³) was synthesized by addition of phenylmagnesium bromide to the unhindered carbonyl group of desylacetophenone and cyclodehydration of the resulting keto alcohol VI³ (which in solution slowly equilibrates with the 2hydroxytetrahydrofuran⁵). This 4,5-dihydrofuran under irradiation^{2b} in benzene reacted differently from the

⁽¹⁾ This work was supported by (a) a National Science Foundation Research grant and (b) a Philip Francis du Pont Fellowship (1963-1964).

^{(2) (}a) R. E. Lutz, J. I. Dale. and D. W. Boykin, Jr., J. Am. Chem. Soc., **85**, 2340 (1963). The isomeric ketone V expected also as a product from this reaction has now been isolated (ca. 25%). (b) Handvia high-pressure mercury arc lamp (450-w.), Pyrex filter.

^{(4) (}a) R. E. Lutz, R. G. Bass, and D. W. Boykin, Jr., J. Org. Chem., in press. The ketone V was shown not to be intermediate in the photo-chemical conversion $I \rightarrow 111$; it reacted but behaved quite differently under the conditions involved, and the products are currently under investigation. (b) Cf. H. E. Zimmerman and D. I. Schuster, J. Am. Chem. Soc., 84, 4527 (1962).

^{(5) (}a) This new and unique example of ring-chain tautomerism with a well-balanced equilibrium is important because it is a favorable one for the further detailed and quantitative study now in progress on the effects of temperature, solvent, and substituents; cf. (b) R. E. Lutz. C. L. Dickerson, and W. J. Welstead, Jr., J. Org. Chem., **27**, 3062 (1962); (c) J. I. Dale, Ph.D. Dissertation, University of Virginia, 1962; (d) P. Bladon and W. McKeekin, J. Chem. Soc., 3504 (1961); (e) G. Eglinton in "Physical Methods in Organic Chemistry," J. C. P. Schwartz, Ed., Oliver and Boyd Ltd., Edinburgh, 1964.