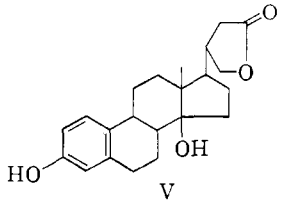
Fermentation of strophanthidin by the general procedure previously described,[1] with *Nocardia restrictus*, produced two principal transformation products. Paper chromatography[2] revealed that both were less polar than strophanthidin. Separation was effected by chromatography upon silica gel and fractional crystallization. The product with higher R_f was characterized as the anhydrostrophanthidone II.[1,3] The second product was a new phenolic compound (III), m.p. 263–265° dec., $[\alpha]^{27}D$ +78° (*c* 0.76, pyr.); λ_{max}^{alc} 217 mμ (ε 25,600), 280 mμ (ε 2,200); λ_{max}^{Nujol} 2.88 μ, 3.03 μ, 5.77 μ, 6.22 μ, 6.30 μ, 6.68 μ.[4] Acetylation of III yielded a monoacetate, m.p. 206–208°, $[\alpha]^{25}D$ +66° (*c* 0.70, chf.); λ_{max}^{MeOH} 215 mμ (ε 22,100), 267 mμ (ε 680), 275 mμ (ε 640); λ_{max}^{chf} 2.88 μ; 5.60 μ, 5.72 μ, 6.15 μ, 6.30 μ, 6.70 μ. Catalytic hydrogenation of III with platinum (hydrogen consumption: 1 mole equivalent) yielded the dihydro derivative V, characterized by direct comparison with a



V

sample prepared from dihydrostrophanthidin by the procedure of Turner and Meschino.[5] Catalytic oxidation of I in the presence of platinum and oxygen, followed directly by treatment with alkali at 0°, yielded the 19-noranhydrostrophanthidone IV, m.p. 240–241°, $[\alpha]^{27}D$ +33° (*c* 2.67, chf.); λ_{max}^{chf} 2.85 μ, 5.60 μ, 5.72 μ 6.01 μ, 6.15 μ; λ_{max}^{EtOH} 230 mμ (ε 24,700). Dehydrogenation of IV over palladium black in refluxing ethanol gave phenol III.

When anhydrostrophanthidone II was exposed to *N. restrictus*, a rapid and high-yield conversion to phenol III was observed. Fermentation of the 19-noranhydrostrophanthidone IV under the same conditions resulted in exceedingly slow conversion to phenol III. These findings are in good agreement with the recent studies of Morato, *et al.*,[6] on the biosynthesis of estrogens from androgens with human placental microsomes. The latter authors' observations support the sequence Δ^4-androstenedione → 19-hydroxyandrostenedione → 19-oxo-androstenedione →·····> estrone for the steps in biological estrogen formation. Furthermore, it was found that 19-norandrostenedione was a poor substrate for estrogen formation. The parallel findings in the respective studies that the 19-nor-steroids are less effective phenol-precursors than the corresponding 19-oxo-steroids suggest that the stepwise sequence may be similar for the microbiological and placental microsomal transformations. Work is currently under way to evaluate the hypothesis that biological conversion of II to III may proceed *via* Δ^1-dehydrogenation to a 19-oxo-$\Delta^{1,4}$-dienone and then aromatization accompanied by liberation of a C_1 unit.[7]

This work was supported by grants from the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

(2) H. R. Urscheler, Ch. Tamm and T. Reichstein, *Helv. Chim. Acta*, **38**, 897 (1955).

(3) A. Katz, *ibid.*, **40**, 831 (1957).

(4) Satisfactory analytical data were obtained for the new compounds reported herein.

(5) R. B. Turner and J. A. Meschino, *J. Am. Chem. Soc.*, **80**, 4862 (1958).

(6) T. Morato, M. Hayano, R. I. Dorfman and L. R. Axelrod, *Biochem. Biophys. Res. Comm.*, **6**, 334 (1961).

(7) Formaldehyde has recently been identified as appearing in stoichiometric ratio to estrone after placental microsomal aromatization of Δ^4-androstenedione and 19-hydroxyandrostenedione (H. Breuer and P. Grill, *Z. physiol. Chem.*, **324**, 254 (1961)). However, in view of the facile biological interconversion of formaldehyde and formic acid (*cf.* F. M. Huennekens and M. J. Osborn, *Adv. in Enzymology*, **21**, 369 (1959)), it is possible that the formaldehyde may have arisen by reduction of a formic acid-equivalent.

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SYNTHESIS OF BORON NITRIDE

Sir:

A broad resemblance of boron nitride to carbon in its various structural forms,[1,2] combined with certain physical characteristics, makes boron nitride a material of considerable theoretical interest and of growing importance in nuclear, refractory, electrical and lubrication technologies. While the synthesis of boron nitride has been studied fairly extensively,[3,4-8] current synthetic methods are beset with considerable technical difficulties. Accordingly, a straightforward synthesis adaptable to laboratory or large-scale production of boron nitride is of interest.

Orthoboric acid (1 mole) and urea (2 moles) are mixed and gradually heated. At about 60° the reactants melt with the evolution of water which is removed from the system in a stream of nitrogen or, preferably, under reduced pressure. As water is removed, the initially limpid liquid residue increases in viscosity and sets to a glass. Above about 165° (subsequent heating is most conveniently effected in a nitrogen stream) the glass undergoes decomposition, evolving a volatile sublimate and leaving a white, cinder-like residue (residue at 600° is 18.45 wt. % urea and boric acid reactants. *Anal.* B, 31.6; N, 20.5; remainder oxygen with only traces of carbon or hydrogen). Further heating of this BNO residue at temperatures up to 1300° does not yield a "boron nitride" of substantially improved purity. Thus, the very early claim of Darmstadt[9] to have prepared boron

(1) R. S. Pease, *Acta. Cryst.*, **5**, 356 (1952).

(2) R. H. Wentorf, *J. Chem. Phys.*, **26**, 956 (1957); U. S. Patent 2,947,617 (Aug. 2, 1960).

(3) K. M. Taylor, *Ind. Eng. Chem.*, **47**, 2506 (1955); U. S. Patent 2,808,314 (Oct. 1, 1957).

(4) R. Taylor and C. A. Coulson, *Proc. Phys. Soc.*, **A65**, 834 (1952).

(5) A. A. Giardini, U. S. Bureau of Mines Information Circular 7664.

(6) G. H. Fetterley and G. R. Watson, U. S. Patent 2,801,903 (Aug. 6, 1957).

(7) L. A. Conant and E. F. Hittle, Canadian Patent 582,108 (Aug. 25, 1959).

(8) F. H. May and V. V. Levasheff, U. S. Patent 2,824,787 (Feb. 25, 1958).

(9) M. Darmstadt, *Lieb. Ann.*, **151**, 255 (1869).

nitride by heating urea and boric acid appears implausible. However, when this BNO residue is heated in a stream of ammonia over the temperature range 500–950°, it is nitrided, with the simultaneous formation and removal of water, to give a relatively pure boron nitride (residue at 950°, 13.63% urea and boric acid reactants. *Anal.* B, 43.9; N, 54.2). This nitridation is significant in that the rate of nitridation progressively increases over the temperature range of 500–950°. This is in contrast to currently favored routes where a viscous boric oxide liquid on a preformed boron nitride or a calcium phosphate support shows slower rates of nitridation. This latter process is substantially unaffected by increasing temperatures over this temperature range. The final traces of oxide impurity may be removed from the boron nitride product by reaction with ammonia at higher temperatures or by heating in a nitrogen stream to 1650°, where the oxide impurity volatilizes (analysis B, 44.2; N, 56.0).

A wide range of nitrogenous materials may be substituted for urea in this reaction scheme, such as biuret, guanidine, cyanamide, dicyandiamide, thiourea, ammelide, and melamine. The nitrogen contents of the solid intermediates and the final products show some variations, but the products obtained using cyanamide, dicyandiamide or guanidine are comparable or superior to that obtained using urea.

In coöperation with N. E. Weston and J. Thomas, Jr., in a paper to be published in the *J. Am. Chem. Soc.*, a turbostatic structure has been found for BN prepared from urea–boric acid and ammonia; a transformation of this structure to the ordered layer lattice occurs, a process which is unexpectedly promoted by boron oxide impurities.

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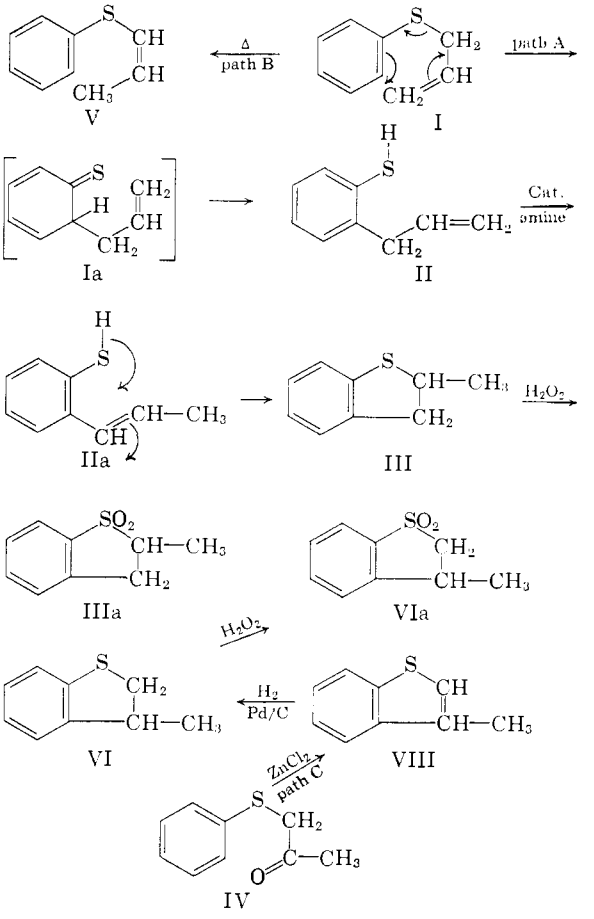
THE CLAISEN REARRANGEMENT OF ALLYL ARYL SULFIDES

Sir:

Failure to produce Claisen rearrangement of allyl thiophenyl ether (I) under conditions[1] which can readily effect the rearrangement of the corresponding oxyethers at reasonable rates[2,3] has been noted recently.[4] The Russian authors of this report have stated that the principal product of the reaction studied earlier by Hurd and Greengard[5] was the consequence of thermally induced prototropic isomerization to the propenyl thiophenyl ether (V) and no more than a trace of *o*-allylthiophenol (II) was found. This result has been attributed to the (assumed) inability to form the dienone intermediate (IA), analogous to that which has been established[6,7] for the Claisen oxyether rearrangement (path A) because of the recognized weakness of the π bond in $\backslash C{=}S$ and the instability of π links composed of other than L valence electrons[8].



We have also observed the formation of (V), the thermal isomerization product, but we have been unable to detect any product resembling (II) under all the reaction conditions previously tried. However, we have now ascertained that on subjecting solutions of allyl thiophenyl ethers containing N,N′-diethylaniline or quinoline to distillation at atmospheric pressures entirely different results are observed. Under these conditions a new product is obtained which is isomeric with (I) and (V) and is not identical with either of the geometric isomers of (V). Furthermore, the new product occurs in 15–20% conversion from a single distillation, alongside of mostly the unreacted allyl thiophenyl

(1) For a full discussion of this reaction see D. S. Tarbell in R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1944, Chapter I.

(2) W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

(3) H. L. Goering and R. R. Jackson, *ibid.*, **80**, 3277 (1958).

(4) E. N. Karaulova, D. Sh. Meilanova and G. D. Gal'pern, *Doklady Akad. Nauk S.S.S.R.*, **113**, 1280 (1957); *Zhur. Obshchei Khim.*, **27**, 3034 (1957).

(5) (a) C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **72**, 3356 (1930). (b) See also, H. D. Hartough and S. L. Meisel, "Compounds with Condensed Thiophene Rings," Interscience Publishers, Inc., New York, N. Y., 1954, p. 35, and W. H. Taylor, *J. Am. Chem. Soc.*, **58**, 2649 (1936).

(6) H. Conroy and R. A. Firestone, *ibid.*, **75**, 2530 (1953); *cf.* also F. Kalberer and H. Schmid, *Helv. Chim. Acta*, **40**, 13, 255, 779 (1957).

(7) D. Y. Curtin and H. W. Johnson, Jr., *ibid.*, **96**, 2276 (1954).

(8) N. Lozac'h, *Record of Chem. Prog.*, **20**, 23 (1959).