values: liquid sulfur at elevated temperatures[5] has a g-value of 2.024 and the blue oleum solutions of sulfur contain two radical species with g-factors of 2.016 and 2.026.[3] The similarity of the g-values of the radicals in these three systems suggests that the paramagnetism of ultramarine may arise from some type of sulfur radical. The concentration of sulfur in an ultramarine is estimated to be 20×10^{-4} g.-atoms/g., on the basis of an average empirical formula $Na_9Al_6Si_6O_{24}S_2$. A rough intensity measurement of the paramagnetic absorption in sample (a) gave an order of magnitude estimate of 4×10^{-4} g.-atoms/g. for the concentration of unpaired electrons; samples (b), (c) and (d) have about this same concentration of radical. It is possible, however, that the paramagnetism is caused by the presence of paramagnetic ions of the transition metals, and this notion was tested by qualitative arc spectrographic analysis of samples (c) and (d). No transition metals except titanium, iron and copper were detected, and these were present in only trace amounts. The observed intensity of paramagnetism is thus of the correct order of of magnitude to be accounted for by sulfur radicals and appears to be much greater than could be attributed to the quantity of heavy-metal impurities present.

Stronger evidence than this for the origin of the paramagnetism could probably be obtained by an investigation of ultramarines in which the sulfur had been replaced by selenium and tellurium, since, if the paramagnetism in ultramarine does arise from sulfur, the substitution of selenium and tellurium should give rise to paramagnetic spectra with characteristically different g-values.

We wish to thank J. M. Nelson for the gift of samples (a), (b) and (f) and T. P. Sciacca for the sample of lazurite. We wish to thank J. A. Dunbar for performing the spectrographic analysis.

(5) D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **76**, 5891 (1954), and unpublished results.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY — DONALD M. GARDNER
NEW YORK 27, NEW YORK — GEORGE K. FRAENKEL

RECEIVED NOVEMBER 7, 1955

FORMATION OF 6-FURFURYLAMINOPURINE FROM DNA BREAKDOWN PRODUCTS

Sir:

A compound, 6-furfurylaminopurine (kinetin), isolated from commercial DNA has been shown[1,2] to bring about cellular proliferation in fragments of tobacco pith when used in conjunction with 3-indoleacetic acid. This compound was found to be growth promoting for a strain of carrot tissue (clone II)[3] at a concentration of 0.1 γ/cc. in presence of three co-factors, coconut milk filtrate, 7 mg./cc., 3-indoleacetic acid, 1 γ/cc., and thiamine 0.1 γ/cc. Using this assay the original observation[1] was confirmed that 6-furfurylaminopurine is present in samples of commercial DNA several years old or solutions of fresh commercial DNA autoclaved at pH 4.3 at 15 lb. for 30 minutes.

(1) C. O. Miller, *et al.*, THIS JOURNAL, **77**, 1392 (1955).
(2) C. O. Miller, *et al.*, *ibid.*, **77**, 2662 (1955).
(3) Full biological details will be published elsewhere.

The purpose of the present work was to determine whether 6-furfurylaminopurine occurs in DNA as such or whether it is formed from natural constituents of DNA. A solution of 1 g. (7.4 mmoles) of adenine and 1 g. (7.4 mmoles) of 2-deoxy-D-ribose in 50 cc. of 0.148 M phosphate buffer (pH 4.0) was autoclaved at 15 lb. for 30 minutes. This solution at a concentration of 10 γ/cc. in the assay media showed the same biological activity as 0.1 γ/cc. of 6-furfurylaminopurine. After removal of phosphate ions by addition of 2.4 g. of barium acetate the reaction product was partitioned on a column containing 100 g. of cellulose powder with water–n-butyl alcohol–1% concentrated ammonia. The biologically active fraction was passed through a column of Dowex-1 × 4 (200–400 mesh, formate cycle). After removal of some adenine and other compounds with 0.01 M formate solution (pH 8.0), 5.4 mg. of crystalline 6-furfurylaminopurine was eluted by 0.01 M formic acid. This sample isolated in 0.54% yield melted at 266–267°. On admixture with an authentic sample of 6-furfurylaminopurine,[4] the melting point was not depressed. Further, the isolated sample had the same ultraviolet absorption curves in dilute acid, neutral solution and dilute alkali, and the same R_f values on paper in six separate solvent systems as authentic 6-furfurylaminopurine.

Solutions of deoxyadenosine, or of furfuryl alcohol and adenine, after autoclaving at pH 4.0 at 15 lb. for 30 minutes became strongly biologically active. The latter solution was found to contain 6-furfurylaminopurine in 2% yield by a procedure similar to that above.

That 6-furfurylaminopurine was not a natural constituent of salmon sperm DNA was shown by behavior of a highly polymerized sample prepared from salmon sperm by the method of Dounce.[5] This sample had no growth-promoting activity for clone II carrot tissue either before or after autoclaving at pH 4.6 at 15 lb. for 30 minutes.

It was therefore concluded that 6-furfurylaminopurine in autoclaved commercial DNA was artificially formed by interaction of adenine and 2-deoxy-D-ribose.

(4) This sample was synthesized by Dr. M. W. Bullock of this Laboratory.
(5) A. Dounce, *et al.*, THIS JOURNAL, **74**, 1724 (1952).

AMERICAN CYANAMID COMPANY
RESEARCH DIVISION — ROSS H. HALL
LEDERLE LABORATORIES — R. S. DE ROPP
PEARL RIVER, NEW YORK

RECEIVED SEPTEMBER 23, 1955

A NEW MODIFICATION OF BORON MONOXIDE

Sir:

During the course of investigations not primarily concerned with boron–oxygen compounds, we have had occasion to prepare sub-boric acid, $B_2(OH)_4$, and to observe its conversion, by dehydration, into a hitherto unreported form of boron monoxide, BO. The latter substance can, in turn, be converted into the reported form[1,2] by either of two paths,

(1) R. C. Ray and P. C. Sinbe, *J. Chem. Soc.*, 742 (1941).
(2) E. Zintl, W. Morawietz and E. Gastinger, *Z. anorg. allgem. Chem.*, **245**, 8 (1940).

one of which involves a surprisingly large amount of energy.

Sub-boric acid, prepared in quantitative yield by the action of water vapor on diboron tetrachloride at room temperature, is a white, microcrystalline solid which starts to lose water at about 90° *in vacuo*.

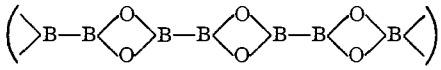
$$B_2(OH)_4 \longrightarrow 2BO + 2H_2O$$

To remove the last traces of water, however, heating for four hours at 220° is required. (1.124 mmoles of $B_2(OH)_4$ treated in this manner liberated 2.278 mmoles of water.) The boron monoxide thus prepared is not light brown as reported by previous workers, but white, and appears substantially unchanged at temperatures up to about 500°. At 650°, *in vacuo*, its color changes to light brown. This latter material, in agreement with previous observation, is only sparingly soluble in water, and solutions thus prepared readily decolorize permanganate.

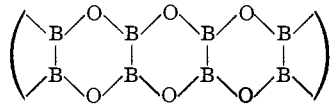
If the white, solid boron monoxide has not been completely dehydrated, its behavior on conversion to the brown form is quite remarkable. Thus, samples which have the approximate composition $BO \cdot {}^1/_{10}H_2O$, when briefly heated to about 400° *in vacuo*, undergo a rapid and spontaneous change, the energy of which is sufficient to heat the entire solid to incandescence. (Using brightness as a criterion, the temperature was estimated at from 700 to 900°.) This behavior has been repeatedly confirmed. The light brown solid which results has the same properties as, and is presumably identical with, the previously prepared light brown material. Also formed are small amounts of hydrogen and a white solid, presumably boric acid but not present in amounts great enough for identification. These latter probably result from thermal decomposition of residual sub-boric acid.

Unlike the white form, the light brown boron monoxide is hard and brittle. Aside from color, the chief observed difference between the two modifications lies in their solubilities in water and methanol, in each of which the white form is readily soluble and the brown form only sparingly so. Prolonged exposure to air does not seem to alter the color or reducing properties of either modification.

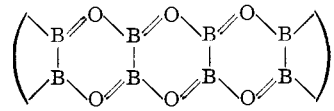
Although arguments for the existence of boron monoxide as B_2O_2 molecules have been presented, its properties do not seem consistent with this interpretation. It seems more likely that boron monoxide, in both modifications, is polymeric. Since one of the forms is white, and the other colored, it may be reasonable to assign to the former the structure



and to the latter the structure



Possible contributions to the latter by quinoid structures, such as



may account for the observed coloration.

The role of water in lowering the temperature of conversion from the white to colored form is not readily explained.

THE PENNSYLVANIA STATE UNIVERSITY
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UNIVERSITY PARK, PA. EUGENE F. APPLE[3]

RECEIVED OCTOBER 26, 1955

(3) General Electric Co., P. O. Box, 1088, Schenectady, N. Y.

THE ADRENAL HORMONES AND RELATED COMPOUNDS. III. SYNTHESIS OF 2-ALKYL ANALOGS[1]

Sir:

Chemical and microbiological modification of the structures of adrenal cortical hormones by the introduction of 9α-halogen or the 1-double bond has resulted in products of high activity.[2] We now report the synthesis of novel 2-alkyl analogs of the adrenal hormones. This modification has resulted in certain cases in marked enhancement of adrenal cortical activity.

11β,21-Dihydroxy-4,17(20)-*cis*-pregnadiene-3-one 21-acetate (I)[3] was treated with ethyl oxalate and methanolic sodium methoxide in *t*-butyl alcohol to form the sodium enolate of 2-ethoxyoxalyl-11β,-21-dihydroxy-4,17(20)-*cis*-pregnadiene-3-one (II) in essentially quantitative yield. Acidification of an aqueous solution of II with dilute hydrochloric acid precipitated the free enol III as an amorphous solid, m.p. 80–100°. Either II or III, when methylated with methyl iodide and potassium carbonate in acetone, followed by removal of the ethoxyoxalyl group by sodium methoxide in methanol, gave 11β,21-dihydroxy-2-methyl-4,17(20)-*cis*-pregnadiene-3-one (IV), m.p. 162.5–164°. *Anal.* Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.64; H, 9.51. Acetylation of IV gave the corresponding 21-acetate V, m.p. 182–184.5°, $[\alpha]_D$ +145° (chl.), λ_{max}^{EtOH} 242 mμ(15,025). *Anal.* Calcd. for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.32; H, 8.79. The yield from II to V was 33%. It seems likely that the 2-methyl group in V is α-oriented or *quasi-equatorial* both because of its method of preparation and because it was not isomerized by further treatment with sodium methoxide in methanol. Oxidation of V by the method of Miescher and Schmidlin[4] or better with phenyl iodosoacetate[1,3] and a catalytic amount of osmium tetroxide gave a mixture of 11β,17α,21-trihydroxy-2-methyl-4-pregnene-3,20-dione 21-acetate (VI), m.p. 133–

(1) Previous paper in this series: J. A. Hogg, F. H. Lincoln, A. H. Nathan, A. R. Hanze, B. J. Magerlein, W. P. Schneider, P. F. Beal and J. Korman, THIS JOURNAL, **77**, 4438 (1955).

(2) (a) J. Fried and E. F. Sabo, *ibid.*, **75**, 2273 (1953); **76**, 1455 (1954); (b) H. L. Herzog, A. Nobile, S. Tolksdorf, W. Charney, E. B. Hershberg, P. L. Perlman and M. M. Pechet, *Science*, **121**, 176 (1955); (c) R. F. Hirschmann, R. Miller, R. E. Beyler, L. H. Sarett and M. Tishler, THIS JOURNAL, **77**, 3166 (1955).

(3) J. A. Hogg, P. F. Beal, A. H. Nathan, F. H. Lincoln, W. P. Schneider, B. J. Magerlein, A. R. Hanze and R. W. Jackson, *ibid.*, **77**, 4436 (1955).

(4) K. Miescher and J. Schmidlin, *Helv. Chim. Acta*, **33**, 1840 (1950).