COMMUNICATIONS TO THE EDITOR

MANY-MEMBERED CARBON RINGS. XIII. RING CLEAVAGE *VIA* 1,4-TRANSANNULAR ELIMINATION IN CYCLOALKANE DERIVATIVES

Sir:

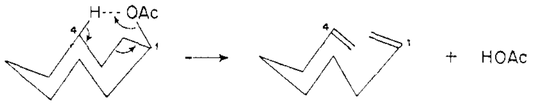
In studying elimination reactions of simple derivatives of medium-sized cycloalkanes we have found that passage of cyclononyl acetate[1] at 500 ± 5° over carborundum chips gives a pyrolysate (78%) comprising 70% 1,8-nonadiene (I) (b.p. 142–144° (740 mm.), $n^{20}\text{D}$ 1.4280, d^{23}_4 0.748. *Anal.* Calcd. for C_9H_{16}: C, 87.10; H, 12.90. Found: C, 86.81, 87.11; H, 13.09, 13.28) and 25% cyclononene (II) (b.p. 172–174.5° (atm.), $n^{25}\text{D}$ 1.4775).[2] Analysis of the latter by an infrared method similar to that used for cyclodecene[3] indicated that it contained 4.8% *trans*-II and 88.6% *cis*-II.

The properties of I were in good agreement with those given by other workers: van Pelt and Wibaut[4] reported b.p. 141–144°, $n^{20}\text{D}$ 1.4302, d^{20}_4 0.751, while Everett and Kon[5] found b.p. 140°, $n^{20}\text{D}$ 1.4275, d^{24}_4 0.740. The diene I obtained by pyrolysis of 1,9-nonanediol diacetate showed b.p. 136–138° (740 mm.), $n^{20}\text{D}$ 1.4270, d^{23}_4 0.741. The infrared spectra of the two samples of I were identical. Quantitative catalytic reduction of I required 106% of two molar equivalents of hydrogen. Oxidative ozonolysis of I afforded pimelic acid (18%) which did not depress the m.p. of authentic pimelic acid.

Similar thermal decomposition of cyclononanol gave a pyrolysate (41%) comprising *ca.* 30% I, $n^{25}\text{D}$ 1.4285, and *ca.* 60% II, $n^{25}\text{D}$ 1.4760. The infrared spectrum of this I was identical with the spectrum of I obtained previously. The infrared spectrum of II obtained here indicated the presence of 10% *trans*-II and 77% (?) *cis*-II. Pyrolysis of II (90% *cis* and 5% *trans*) with acetic acid gave *ca.* 19% I and 50% II (all *cis*).

Cycloöctyl and cyclodecyl acetates also undergo a similar ring opening on pyrolysis (500°) but to a lesser extent. From the former *ca.* 10% of 1,7-octadiene, $n^{20}\text{D}$ 1.4328–1.4366, is obtained while the latter gives *ca.* 20% of 1,9-decadiene, $n^{25}\text{D}$ 1.4335. The infrared spectrum of this decadiene is identical with the spectrum of 1,9-decadiene formed in the pyrolysis of 1,10-decanediol diacetate.

It is suggested that the ring cleavage of the cycloalkyl acetates to terminally unsaturated open-chain dienes involves a transannular 1,4-elimination of acetic acid. Conformations of the cycloalkyl acetates having the acetoxy group in a *quasi-axial* position (O-inside) may form a six-membered ring transition state intermediate transannularly. Involved in this are a *quasi-axial* hydrogen attached to a carbon atom in the number four position and the ethereal oxygen atom of the *quasi-axial* acetoxy group. This elimination appears to be particularly facile in the nine-membered ring.



Some evidence is accumulating which indicates that 1,4-elimination of acetic acid may also occur in the pyrolysis of certain acetoxy derivatives of smaller carbocycles. In these instances also the structural features are such that a 1,4-transannular formation of a six-membered ring transition state intermediate is possible. A subsequent paper will present these observations.

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(1) M. Kobelt, D. Bauman, V. Prelog and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949).

(2) A. T. Blomquist, L. H. Liu and J. C. Bohrer, THIS JOURNAL, **74**, 3643 (1952).

(3) A. T. Blomquist and A. Goldstein, *ibid.*, **77**, 1001 (1955).

(4) A. J. van Pelt, Jr., and J. P. Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

(5) J. Everett and G. Kon, *J. Chem. Soc.*, 3131 (1950).

(6) Du Pont Post-Graduate Teaching Fellow.

PARAMAGNETIC RESONANCE OF ULTRAMARINE[1]

Sir:

The blue color of the ultramarines has been the subject of much investigation and speculation for many years and, although it has been generally agreed that this color is due to the presence of sulfur, the nature of the sulfur component has never been elucidated.[2] An analogy between this color and the color of solutions of sulfur in oleum has been suggested, and since the oleum solutions have recently been found to be paramagnetic,[3] we attempted to detect a paramagnetic resonance absorption in the ultramarines.

Both natural and synthetic ultramarines were found to exhibit a paramagnetic resonance spectrum.[4] In the following tabulation the values of line width are the separations in gauss between points of inflection of the absorption line, and the *g*-value are the spectroscopic splitting factors.

Sample	Source of ultramarine	Line width	*g*-Value
a	Synthetic material, origin unknown	17	2.028
b	French Laundry Blue, John B. Wade, N. Y.	18	2.029
c	Bleachette Laundry Blue, American Cyanamid Co.	19	2.028
d	Rickett's Paris Blue, F. T. French Co.	23	2.029
e	Lazurite, North Carolina	*ca.* 100	2.02
f	Synthetic material, origin unknown	*ca.* 700	2.13

Two other systems in which the paramagnetism has been identified with sulfur have similar *g*-

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(1) Supported in part by the Squier Signal Laboratory, U. S. Army Signal Corps.

(2) W. Eitel, "The Physical Chemistry of the Silicates," University of Chicago Press, Chicago, Ill., 1954, pp. 810–815.

(3) D. M. Gardner and G. K. Fraenkel, unpublished results.

(4) The paramagnetic resonance measurements were performed at a wave length of 3.2 cm. with the spectrometer described by J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.*, **26**, 34 (1955).

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.

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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.

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.

[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.

[4] This sample was synthesized by Dr. M. W. Bullock of this Laboratory.

[5] A. Dounce, *et al.*, THIS JOURNAL, **74**, 1724 (1952).

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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).