COMMUNICATIONS TO THE EDITOR

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

Sir:

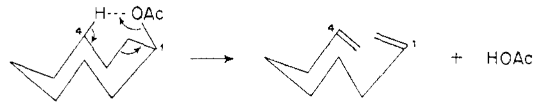
In studying elimination reactions of simple derivatives of medium-sized cycloalkanes we have found that passage of cyclononyl acetate[1] at 500 ± 5° over carborundum chips gives a pyrolysate (78%) comprising 70% 1,8-nonadiene (I) (b.p. 142–144° (740 mm.), n^{20}_{D} 1.4280, d^{23}_{4} 0.748. *Anal.* 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}_{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}_{D} 1.4302, d^{20}_{4} 0.751, while Everett and Kon[5] found b.p. 140°, n^{20}_{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}_{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}_{D} 1.4285, and *ca.* 60% II, n^{25}_{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}_{D} 1.4328–1.4366, is obtained while the latter gives *ca.* 20% of 1,9-decadiene, n^{25}_{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).