include (1) a N/P ratio of 3.7 ± 0.3, (2) a specific refractive index increment at $\lambda = 436$ mμ of 0.193 ± 0.004 and (3) a partial specific volume of 0.68 ± 0.01.

Measurement	DNP	DNA
Molecular weight (light scattering)	$19 \pm 4 \times 10^6$	$8 \pm 2 \times 10^6$
Radius of gyration (light scattering), Å.	1700 ± 200	2900 ± 300
Intrinsic viscosity (100 cc./g.)	35 ± 2	70 ± 10
Sedimentation constant, S^{w}_{20}	50 ± 5	22 ± 2
Flow birefringence,[a] Å.	4800–3000	14,000–9,000

[a] The values given are the range of apparent lengths calculated from the extinction angle assuming a rigid ellipsoid model. This provides a rough *estimate* of the polydispersity and the maximum dimension of the coiled particles.

Inasmuch as the yield of DNP accounts for the majority of DNA in the thymus, it appears that the particles isolated and studied here may be the principal structural units of chromosomes. A study of the organization of the DNA and protein in the DNP particle will be reported soon.

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(5) U. S. Public Health Service Predoctorate Research Fellow of the National Heart Institute.

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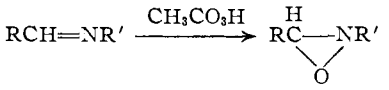
RECEIVED SEPTEMBER 19, 1956

THE SYNTHESIS OF OXAZIRANES

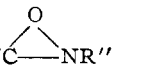
Sir:

We have observed recently that certain azomethines which are sluggish toward acid hydrolysis may be oxidized readily in good yield with anhydrous peracetic acid in methylene chloride to compounds whose structures are best formulated as oxaziranes. These materials appear to be the first obtained with a well-authenticated oxygen–nitrogen–carbon three-membered ring system.[1,2]



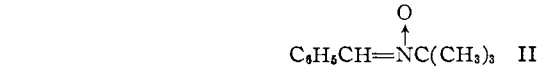
They are active oxygen compounds comparable in many respects to organic peroxides and indeed may be assayed by iodometric procedures. Typical examples of azomethines which may be converted to oxaziranes are those derived from aldehydes and *t*-carbinamines[3] and those obtained from *p*-nitrobenzaldehyde and most amines. The former compounds are resistant to acid hydrolysis because of steric factors and the latter because of electronic effects. The physical properties and yields of some typical oxaziranes are summarized in Table I.

TABLE I

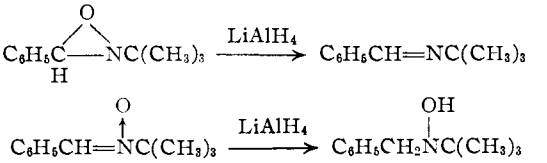
SYNTHESIS OF OXAZIRANES, 

R	R′	R″	B.p. °C.	B.p. Mm.	Yield, %	$n^{20}D$
H	H	*t*-Bu	52	75	46	1.4150
C_6H_5	H	*t*-Bu	63	0.5	71	1.5081
H	H	*t*-Octyl	64	6	69	1.4445
p-$NO_2C_6H_4$	H	Et	34–35	(m.p.)	95	
CH_3	*i*-Bu	*n*-Pr	64	7	63	1.4277

The oxazirane structure of these compounds is based on a number of facts: (1) analytical data, (2) their quantitative hydrolysis to β-alkylhydroxylamines and aldehydes, (3) a comparison of their physical and chemical properties with those of the isomeric nitrones, (4) their conversion to the isomeric nitrones under anhydrous conditions, and finally (5) the partial resolution of 2-*n*-propyl-3-methyl-3-isobutyloxazirane. Most of the structural work was done with 2-*t*-butyl-3-phenyloxazirane (I) since its hydrolysis and reduction products could be conveniently characterized. This material on hydrolysis with sulfuric acid in aqueous methanol gave quantitative yields of benzaldehyde and β-*t*-butylhydroxylamine (m.p. 64°; Found: C, 53.69; H, 12.64; N, 15.47). The availability of β-*t*-butylhydroxylamine permitted the synthesis of the isomeric nitrone (II)



which may properly be regarded as an "electronic tautomer" of the oxazirane. This nitrone melted at 76° (Found: C, 74.60; H, 8.55; N, 7.62), was not an active oxygen compound and had very different properties from the isomeric oxazirane. It absorbed strongly in the ultraviolet (λ_{max}, 225 mμ, ϵ_{max} 6800; λ_{max} 295 mμ, ϵ_{max} 16,700) whereas the corresponding oxazirane showed only that absorption associated with the benzene ring (λ_{max} 249 mμ, ϵ_{max} 930). Reduction of the oxazirane (I) with lithium aluminum hydride in ether yielded only N-benzylidene *t*-butylamine while reduction of the corresponding nitrone under comparable conditions gave benzyl-*t*-butylhydroxylamine (m.p. 72°. Found: C, 73.72; H, 9.77; N, 7.60).



The relationship between the oxazirane and the nitrone also was indicated clearly by the observation that in boiling acetonitrile I was isomerized to II under completely anhydrous conditions. Final confirmation of the oxazirane structure was obtained by partial resolution ($\alpha^{22}D$ −3.94°) of 2-*n*-propyl-3-methyl-3-isobutyloxazirane after incomplete degradation of the compound with

(1) Both nitrones and azoxy compounds have been written as three-membered rings in the older literature. However, no such ring apparently has ever been established with certainty, L. I. Smith, *Chem. Revs.*, **23**, 223 (1938).

(2) The numbering of the oxazirane system is 

(3) M. D. Hurwitz, U. S. Patent 2,582,128, January 8, 1952.

brucine in boiling methylene chloride. Under these circumstances the brucine is converted to the insoluble brucine-N-oxide in quantitative yield.

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ENZYMATIC PHOSPHORYLATION OF D-XYLULOSE IN LIVER

Sir:

L-Xylulose, a naturally occurring sugar found in urine, has been shown to be glucogenic in diabetic dogs although the mechanism has been hitherto unknown.[1] Recently Touster, *et al.*,[2,3] have reported that L-xylulose may be converted to D-xylulose in guinea pig liver. Since D-Xu5P[4] is readily converted to G 6P,[5,6] it is clear that the phosphorylation of D-xylose in mammalian tissue is the only missing step in the formation of glucose from L-xylulose. The present finding of D-xylulokinase in liver completes this reaction sequence and supports the hypothesis of Touster which may be formulated as

$$\text{L-xylulose} \xrightarrow[\text{TPNH}]{} \text{xylitol} \xrightarrow[\text{DPN}]{}$$

$$\text{D-xyluose} \xrightarrow{\text{ATP}} \text{D-Xu5P} \underset{\text{cycle}}{\overset{\text{Pentose}}{\rightleftharpoons}} \text{G 6P} \longrightarrow \text{glucose}$$

TABLE I

ASSAY OF THE D-XYLULOKINASE REACTION PRODUCTS

Component	Phosphate ester formed[a] μmoles	Dephosphorylated sugar recovered[e] μmoles
Xylulose	150[b]	100[f]
Ribulose	100[c]	67[g]
Ribose	80[d]	55[g]
Total	330	222

[a] The reaction mixture containing 1000 μmoles each of D-xylulose, ATP and $MgCl_2$ was incubated with 100 mg. of the enzyme preparation in a total volume of 150 ml. of 0.02*M* triethanolamine buffer, *p*H 7.6, for 30 minutes at 37°. The reaction was stopped with perchloric acid and the supernatant treated with Norite to remove the adenine nucleotides. The filtrate was neutralized and the sugar phosphates precipitated by the addition of barium acetate and ethanol. The dry barium salt contained 360 μmoles of total phosphorus and 30 μmoles of inorganic phosphorus. [b] Xu5P was determined by a specific enzymatic assay employing rat liver transketolase and triosephosphate dehydrogenase.[7] [c] Ru5P was measured by the cysteine–carbazole method,[8] allowance being made for the Xu5P present. [d] R5P was assayed by the phloroglucinol reaction of Dische.[9] [e] Further confirmation of the identity of the reaction products was obtained by enzymatic dephosphorylation and isolation of the free sugars by Dowex-1 borate chromatography as previously described.[10] [f] Xylulose was identified by its characteristic reaction in the cysteine-carbazole and orcinol reaction, its optical rotation, $\alpha^{24}D$ −33° (H_2O, *c* 1.35), its behavior on paper chromatography in saturated phenol–water, and by the formation of a crystalline *p*-bromophenylhydrazone, the melting point of which remained unchanged at 126–128° when mixed with a similar derivative prepared from authentic D-xylulose. [g] The ribulose fraction exhibited an optical rotation of $\alpha^{24}D$ −15° (H_2O, *c* 0.90) and the ribose a rotation of $\alpha^{24}D$ −22° (H_2O, *c* 0.45). The identity of both sugars was further checked by paper chromatography and colorimetric analysis as above.

D-Xylulokinase has been purified about 10-fold from a water extract of calf liver acetone powder and shown to be specific for D-xylulose. The preparation was inactive toward D-xylose, L-xylulose, D-ribulose, D-ribose and D-fructose. The partially purified enzyme was free from transketolase but was contaminated with phosphoketopentoepimerase and phosphoribose isomerase. Consequently the over-all reaction observed was

$$\text{D-xylulose} + \text{ATP} \xrightarrow[\text{kinase}]{\text{xylulo-}} \text{D-Xu5P} \underset{}{\overset{\text{epimerase}}{\rightleftharpoons}}$$

$$\text{D-Ru5P} \underset{}{\overset{\text{isomerase}}{\rightleftharpoons}} \text{D-R5P}$$

Following incubation of ATP and D-xylulose with the enzyme preparation, the reaction mixture was found to contain all three phosphate esters in the quantities shown in Table I.

The inability of the enzyme preparation to react with either D-ribose or D-ribulose eliminated the possibility that either of these sugars might have served as substrate with subsequent conversion to D-Xu5P, It is therefore clear that mammalian tissue does possess the complete enzymatic structure necessary to carry out the conversion of L-xylulose to D-glucose as postulated by Touster. The identity of the enzymatic step, or steps, which are lacking in essential pentosuria remains to be determined.

(1) H. W. Larson, W. H. Chambers, N. R. Blatherwick, M. E. Ewing and S. D. Sawyer, *J. Biol. Chem.*, **129**, 701 (1939).

(2) O. Touster, V. H. Reynolds and R. M. Hutcheson, *ibid.*, **221**, 697 (1956).

(3) S. Hollmann and O. Touster, THIS JOURNAL, **78**, 3544 (1956).

(4) These abbreviations are used: D-Xu5P, D-xylulose 5-phosphate; G 6P, glucose 6-phosphate; D-Ru5P, D-ribulose 5-phosphate; D-R5P, D-ribose 5-phosphate; ATP, adenosinetriphosphate; TPNH, reduced triphosphopyridine nucleotide; DPN, diphosphopyridine nucleotide.

(5) P. A. Srere, J. R. Cooper, V. Klybas and E. Racker, *Arch. Biochem. Biophys.*, **59**, 535 (1955).

(6) B. L. Horecker, J. Hurwitz and P. Z. Smyrniotis, THIS JOURNAL, **78**, 692 (1956).

(7) Method to be published elsewhere.

(8) Z. Dische and E. Borenfreund, *J. Biol. Chem.*, **192**, 583 (1951).

(9) The authors are grateful to Dr. Dische for kindly making the details of his method available in advance of publication.

(10) G. Ashwell and J. Hickman, THIS JOURNAL, **76**, 5889 (1954).

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THERMODYNAMIC CALCULATIONS FOR THE Mo–C–H SYSTEM

Sir:

Browning and Emmett[1] have reported on "Equilibrium Measurements in the Mo–C–H System," the equilibria investigated being

$$2\,Mo + CH_4 = Mo_2C + 2H_2 \qquad K_1 = (H_2)^2/CH_4 \quad (1)$$

and

$$Mo_2C + CH_4 = 2MoC + 2H_2 \qquad K_2 = (H_2)^2/CH_4 \quad (2)$$

From a plot of log K_p *vs.* $10^3/T$, °K. for reactions (1) and (2), Browning and Emmett calculated the

(1) L. C. Browning and P. H. Emmett, THIS JOURNAL, **74**, 4773 (1952).