Acid hydrolysis of II followed by acetylation and chromatographic separation[4] yields N-methyl-α-L-glucosamine pentaacetate, $[\alpha]^{29}D$ −99 ± 2° (*c* 1, chloroform), m. p. 158°, unchanged on admixture with an authentic synthetic specimen. These data demonstrate that in streptomycin, the carbonyl group of N-methyl-L-glucosamine is glycosidically joined to the central portion, which is in turn similarly linked to streptidine.

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2,2,5,5-TETRAMETHYL-3-HEXENE

Sir:

The properties of *sym*-di-*t*-butylethylene, as recently reported by Hennion and Banigan,[1] are not in agreement with the properties measured in these laboratories on 2,2,5,5-tetramethyl-3-hexene, nor with those reported by Moersch.[2] However, the properties of the paraffin hydrocarbon (2,2,5,5-tetramethylhexane) prepared from the olefin by each investigator are in close agreement. The properties of the compounds in question are listed in Table I.

TABLE I

	B. p., °C.	F. p., °C.	d^{20}	$n^{20}D$
2,2,5,5-Me$_4$-3-hexene[a] (*trans*)	125.013[b]	− 4.75	0.71673[c]	1.41148[d]
2,2,5,5-Me$_4$-3-hexene[e] (*trans*)	123.2[f]	.....	.7176	1.4117
2,2,5,5-Me$_4$-3-hexene[g] (*cis*)	144.2-144.4[h]	< −65	.7439	1.4271
2,2,5,5-Me$_4$-hexane[a]	137.457[i]	−12.64	.71875[j]	1.40550[k]
2,2,5,5-Me$_4$-hexane[g]	136.2-136.4[l]	−13	.7189	1.4060
2,2,5,5-Me$_4$-hexane[m]	135.8-136.1[n]	−11.6		1.4057

[a] This work. [b] At 760 mm., dT/dP = 0.048°/mm. range (20–80% distilled) = 0.010°. [c] d^{25} = 0.71223. [d] $n^{25}D$ = 1.40890. [e] Moersch, ref. 2. [f] At 727.3 mm. [g] Hennion and Banigan, ref. 1. [h] At 748 mm. [i] At 760 mm., dT/dP = 0.050°/mm. range (20–80% distilled) = 0.004°. [j] d^{25} = 0.71480. [k] $n^{25}D$ = 1.40315. [l] At 739 mm. [m] Buechele, Thesis, Pennsylvania State College, 1937. [n] At 731 mm.

An examination of the experimental evidence reveals that there exists no reasonable doubt concerning the identity of the di-*t*-butylethylene (2,2,5,5-tetramethyl-3-hexene) reported by each investigator. We suggest that the two sets of physical properties may correspond to the two geometric isomers, and that our low-boiling, high-melting olefin is the *trans* isomer, and that of Hennion and Banigan (low-melting, high-boiling) is the *cis* isomer. The methods of preparation strengthen this conjecture. Additional confirmation lies in the fact that the molecular model for *cis*-2,2,5,5-tetramethyl-3-hexene shows very large steric hindrance among four of the methyl groups.

Our synthesis was carried out as follows: 2,2,5,5-Tetramethyl-3-hexanol was prepared by the method described by Moersch.[2] Methyl *t*-butylacetate (6815 g., 52.4 moles) was added to *t*-butylmagnesium chloride (about 300 moles). The product was recovered by orthodox methods and distilled in a 30-plate column. There was obtained 6507 g. (41.2 moles, 79%) of carbinol collected at 166–170°. The carbinol was dehydrated by J. T. Baker Hydralo at 300–305° to a mixture of olefins (4999 g., 86.6%). The mixture was separated into concentrates boiling at 121–127° (2,2,5,5-tetramethyl-3-hexene, 34.5 mole per cent. of product), 139–145° (2,3,5,5-tetramethyl-1-hexene, 35.2%), and 152–158° (2,3,5,5-tetramethyl-2-hexene, 30.2%). The first concentrate was redistilled in a 30-plate column, and the best portion was fractionated in a 6-foot Podbielniak column. Physical constants were measured on a selected best fraction from the latter distillation. Ozonolysis of a sample of 2,2,5,5-tetramethyl-3-hexene gave only trimethylacetaldehyde (m. p. and mixed m. p. of 2,4-dinitrophenylhydrazone, 207–208°).

High-pressure hydrogenation of this olefin gave 2,2,5,5-tetramethylhexane. The other two olefins yielded 2,2,4,5-tetramethylhexane. Purification by distillation in a 6-foot Podbielniak column gave a high-purity sample for measurement[3] of physical constants.

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(1) Hennion and Banigan, THIS JOURNAL, **68**, 1202 (1946).

(2) Moersch, Ph. D. Thesis, Pennsylvania State College, 1942.

(3) Brooks, Howard and Crafton, *J. Research Natl. Bur. Standards*, **23**, 637 (1939).

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2,3-DIAMINOQUINOXALINE

Sir:

Our attention has been called to the publication by Gowenlock, Newbold and Spring, *J. Chem. Soc.*, 622 (1945), describing the preparation of 2,3-diaminoquinoxaline by essentially the same procedure as that described in our recent publication, THIS JOURNAL, **68,** 1035 (1946). We are extremely sorry that we neglected to include this reference in our publication.

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RECEIVED SEPTEMBER 18, 1946

PREPARATION OF 2-THIENYLMETHYLCARBINOL AND α-VINYLTHIOPHENE

Sir:

α-Vinylthiophene was obtained in quantitative yields by dehydrating 2-thienylmethylcarbinol at the boiling point of the alcohol over an open flame. To prevent a possible loss of the monomeric α-vinylthiophene through polymerization in the dehydrating flask, 0.1% hydroquinone was added to the alcohol before dehydration. The temperature of the vapor rose rapidly to 100° and then gradually to 130–135° and remained at this latter temperature until the dehydration was completed. α-Vinylthiophene is a water-like liquid having a styrene-like odor with the following constants: $d^{20}{}_4$ 1.0429, $n^{23.4}{}_{\rm D}$ 1.5612.

α-Vinylthiophene polymerizes at room temperature to a yellowish transparent resin characterized by flexibility despite apparent hardness. The polymer obtained after ninety days was softened by toluene, cyclohexanol, thiophene and acetone at 25° but did not dissolve in any of these solvents. The polymer dissolved slowly in boiling cyclohexanol. Further work is in process on the thermal polymerization of α-vinylthiophene with special reference to degree of polymerization and average molecular weights of the polymer samples.

The 2-thienylmethylcarbinol from which the α-vinylthiophene was obtained was prepared according to the Meerwein–Ponndorf–Verley reduction[1] method: 70.08 g. (0.555 mole) of pure 2-acetylthiophene obtained by fractionally distilling a sample of the ketone as originally supplied by the Socony–Vacuum Laboratories, New York, N. Y., and utilizing the fraction which distilled at 89–90° (9 mm.) in the oxidation–reduction reaction, gave a yield of 44.16 g. (0.344 mole) of the secondary alcohol. Previous work[2] on the preparation of the carbinol reported yields of approximately 47% in contrast to a rectified yield of about 62% for this investigation. During the reduction of the ketone with aluminum isopropylate in dry isopropyl alcohol, the yield of acetone is used as an index of the reaction progression. Kuhn and Dann carried the reaction for only three hours, at which time the acetone test reagent (0.1% solution of 2,4-dinitrophenylhydrazine[3] still gave positive results indicating an incomplete reduction. The present investigation carried the reduction to a negative acetone test after a reaction time of five and one-half hours.

The reaction mixture was gently heated between 82–84° in an oil-bath at 107°. The vapor temperatures varied between 77–81°, becoming progressingly higher at the end of the reaction.

The carbinol is a water-white oil becoming yellowish upon standing and has a pleasantly sweet odor. It was separated from the by-products of the reaction by fractionation in a 10-cm. semimicro Widmer spiral distillation column and that portion which distilled at 88–89° (6 mm.) was used in the preparation of α-vinylthiophene. Additional constants found on 2-thienylmethylcarbinol were as follows: $d^{20}{}_4$ 1.0926, $n^{23.4}{}_{\rm D}$ 1.5419. Two by-products were removed before the alcohol distilled over during the fractionation: 2 ml. of a floral-odor substance distilled at 38–40° (12 mm.), $n^{23}{}_{\rm D}$ 1.4922, and 5.5 ml. of a second substance at 75–78° (12 mm.), $n^{23}{}_{\rm D}$ 1.4862. Approximately 8 ml. of residue remained in the distillation flask.

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[1] Roger Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

[2] von Richard Kuhn and Otto Dann, *Ann.*, **547**, 293–299 (1941).

[3] Lund, *Ber.*, **70**, 1520 (1937).

THE CHARACTERISTIC SHEAR VALUE: A COEFFICIENT OF THIXOTROPIC BREAKDOWN

Sir:

In a recent article[1] equations for thixotropic breakdown in suspensions have been given. For the conditions that (1) the down-curves intersect at a common point and that (2) the up-curve also passes through the common point, the equation of the upcurve can be expressed in the form

$$U/M = \ln k - \ln (\sigma - \sigma_0) \qquad (1)$$

where U is the plastic viscosity, σ is the rate of shear with the subscript 0 referring to the common point, M is the "coefficient of thixotropic breakdown with varying rates of shear," and k is a constant. Based upon eq. 1 Green and Weltmann have introduced a new coefficient, V, designated the "coefficient of thixotropic breakdown when the yield value (f) changes with variation in the plastic viscosity (U)," and given by

$$V = -\,\mathrm{d}f/\mathrm{d}U \qquad (2)$$

This writer wishes to point out that eq. 2 is independent of eq. 1 and that the coefficient V is simply the rate of shear corresponding to the common point. Consider a series of straight lines intersecting the force axis at various points $f_1, f_2, \ldots, f_n$ and passing through a common point whose coördinates of force and rate of shear are f_0 and σ_0, respectively. Then the slope or plastic viscosity of each line is given by

$$U = (f_0 - f)/\sigma_0 \qquad (3)$$

By differentiating eq. 3 and rearranging, one obtains

$$\sigma_0 = -\,\mathrm{d}f/\mathrm{d}U \qquad (4)$$

Thus from eqs. 2 and 4 it is seen that V is equal to σ_0.

In Green's[1] treatment of the problem V was obtained from a series of equations and substitutions from which the following relationships were taken: $V = 2/MJ$, $J = 2S/MC\omega_0$, and $C = S/\ln (R_c/R_b)$. Condensing the various constants

$$V = \frac{\omega_0}{\ln (R_c/R_b)} \qquad (5)$$

For a rotational viscometer in which the separation of the cylinders is small, the average rate of shear can be obtained by assuming a linear velocity gradient between the cylinders, *viz.*

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[1] H. Green and R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed.*, **18**, 167 (1946).