tion of Sn–H bonds. The reaction products were apparently mixtures, containing no detectable amount of triphenylstannane.

Acknowledgment.—The author is grateful to Dr. Eugene G. Rochow for helpful discussions and advice, and to the National Science Foundation for financial support.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF AN ARGINYL PEPTIDE

Sir:

The synthesis of peptides containing arginine has presented unusual difficulties, and only a few dipeptides have been reported. No peptide in which the carboxyl group of arginine is linked to another amino acid has been synthesized.[1] It has now been found that the pyrophosphite method[2] can be used for this purpose.

Carbobenzoxy-L-arginine hydrobromide[3] (0.010 mole) and methyl L-leucinate (0.010 mole) were added to 7 cc. of diethyl phosphite, then tetraethyl pyrophosphite (0.020 mole) was added. After 30 minutes heating on a steam-bath, methyl carbobenzoxy-L-arginyl-L-leucinate hydrobromide hydrate was precipitated as a gum by 100 cc. of anhydrous ether. This was crystallized by dissolving in 5 cc. of methanol, bubbling in hydrogen bromide a moment, then adding 40 cc. of anhydrous ether; yield 3.06 g. (57%). A further 0.47 g. was obtained from the original filtrate on dilution with ether, giving 3.53 g. in all (66%). Solution in 10 cc. of methanol and dilution with 40 cc. of water yielded 2.79 g. (52%), m.p. 90–92°,[4] $[\alpha]^{23}\text{D}\ -20.3°$ (*c* 2, methanol).

Anal. Calcd. for $C_{21}H_{36}N_5O_6Br$: C, 47.2; H, 6.79; N, 13.1; Br, 15.0. Found: C, 47.4; H, 6.99; N, 13.3; Br, 15.2.

Carbobenzoxy-L-arginyl-L-leucine was obtained by heating 2.83 g. of the methyl ester hydrobromide hydrate on a steam-bath in 28 cc. of *N* hydrobromic acid for an hour, making slightly alkaline with ammonium hydroxide and chilling. The crystalline product was recrystallized from 30 cc. of *N*/6 hydrobromic acid by the addition of ammonium hydroxide; yield 1.20 g. (54%), m.p. 223–224° dec., $[\alpha]^{24}\text{D}\ -26°$ (*c* 2, 0.4 *N* HBr). *Anal.* Calcd. for $C_{20}H_{31}N_5O_5$: C, 57.0; H, 7.41; N, 16.6. Found: C, 57.2; H, 7.64; N, 16.6.

L-Arginyl-L-leucine hydrobromide hydrate was obtained by hydrogenation with a palladium catalyst of 1.06 g. of the carbobenzoxy derivative in 40 cc. of water plus 2.5 cc. of 1.04 *N* HBr. A crystalline product obtained by evaporation of the filtered solution under vacuum was washed out with acetone, then recrystallized by dissolving in 4 cc. of water and slowly adding 40 cc. of acetone; yield 0.78 g. (80%), m.p. 162–163° dec., $[\alpha]^{24}\text{D}\ +8.6°$ (*c* 2, water).

Anal. Calcd. for $C_{12}H_{28}N_5O_4Br$: C, 37.3; H, 7.3; N, 18.1; Br, 20.7. Found: C, 37.1; H, 7.2; N, 18.2; Br, 20.7.

Paper chromatography gave an R_f value of 0.58 in a butanol–water–acetic acid (5:4:1) system, and showed the presence of arginine and leucine in an acid hydrolysate.

CHEMOTHERAPY DIVISION
STAMFORD RESEARCH LABORATORIES
AMERICAN CYANAMID COMPANY
STAMFORD, CONNECTICUT

GEORGE W. ANDERSON

RECEIVED SEPTEMBER 2, 1953

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[1] J. S. Fruton, "Advances in Protein Chemistry," Vol. V, Academic Press, Inc., New York, N. Y., 1949, p. 64.

[2] G. W. Anderson, J. Blodinger and A. D. Welcher, THIS JOURNAL, **74**, 5309 (1952).

[3] Prepared by R. Janice Joyce, of these laboratories; m.p. 177–179.5°, $[\alpha]^{24}\text{D}\ -6.9°$ (*c* 2, water); calcd. for $C_{14}H_{21}N_4O_4Br$: 20.8% Br. Found: 20.6% Br.

[4] Melting points were taken on a calibrated Fisher–Johns block.

TWO DIMENSIONAL PHASE TRANSITION OF ETHANE ON SODIUM CHLORIDE

Sir:

The chief evidence for first-order phase transitions of films adsorbed on solid surfaces has been the adsorption isotherms measured by Jura, *et al.*, for *n*-heptane on graphite,[1] ferric oxide[2] and reduced silver powder.[3] Adsorption isotherms for *n*-heptane on the same solids (but not the same samples) have subsequently been repeated by Smith[4] and by Young, Beebe and Bienes,[5] who report that their work provides no evidence of first-order phase transitions in those systems. Their papers support the trend to interpret all experimentally observed discontinuities in adsorption isotherms as caused by slow rates or diffusion inside the sample or errors in the apparatus.

The chief remaining evidence for a first-order phase transition of an adsorbed film on a solid surface now devolves on the adsorption isotherms of ethane on sodium chloride and on potassium chloride crystals at 90°K., reported by Ross and Boyd,[6] and since verified in this laboratory on a different sample of sodium chloride at 90°K. by Mr. W.

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[1] G. Jura, W. D. Harkins and E. H. Loeser, *J. Chem. Phys.*, **14**, 344 (1946).

[2] G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *ibid.*, **14**, 117 (1946).

[3] Jura, *et al.*, *ibid.*, **13**, 535 (1945).

[4] R. N. Smith, THIS JOURNAL, **74**, 3477 (1952).

[5] D. M. Young, R. A. Beebe and H. Bienes, *Trans. Faraday Soc.*, **49**, 1086 (1953).

[6] S. Ross and G. E. Boyd, "New Observations on Two-Dimensional Condensation Phenomena," MDDC Report 864, 1947,

Winkler. In spite of the success of certain conclusions drawn by Ross,[7] based on the hypothesis that the observed discontinuity is due to a first-order transition, the evidence lacked the important further authority that could be provided by results at different temperatures. This communication reports the adsorption isotherms of ethane on sodium chloride crystals at 136.0, 131.3 and 122.9° K. These isotherms confirm the existence of a discontinuity and strongly support its interpretation as a first-order phase transition. Figure 1 shows the three isotherms. The isotherm at 122.9°K., with its marked vertical discontinuity, is still below the "two-dimensional critical temperature." The isotherm at 131.3°K. has a much shorter discontinuity that indicates its proximity to the critical temperature. The isotherm at 136.0° K. has no instantaneous vertical slope,[8] and is above the critical temperature. These three isotherms therefore show critical temperature phenomena in the behavior of the adsorbed film of ethane on sodium chloride.

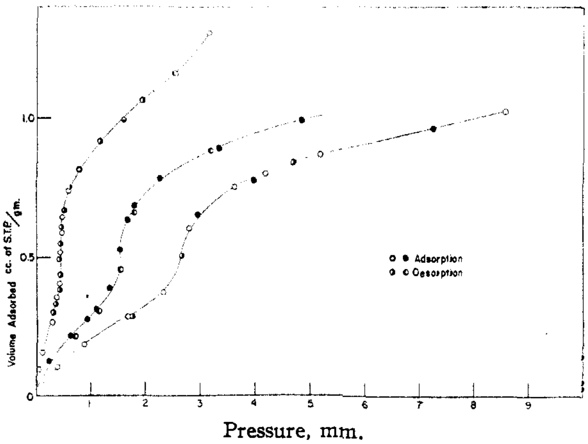

Fig. 1.—Adsorption and desorption of ethane on cube crystals of sodium chloride, at 122.9, 131.3 and 136.0°K.

The two-dimensional critical temperature of ethane on sodium chloride is less than half of the normal three-dimensional critical temperature. This type of behavior has been described by de Boer,[9] as to be expected from the introduction of an induced dipole moment on the ethane molecule from the ionic surface. To cause such a lowering of the two-dimensional critical temperature, the dipoles must be oriented parallel to each other. A diagram illustrating the arrangement of the condensed phase of ethane on a sodium chloride substrate was published by Ross[7] in 1948, and embodies an implicit prophecy of this requirement. Each molecule of ethane is depicted on the crystal lattice in an identical position with respect to the surrounding positive and negative ions. The induced dipoles would therefore necessarily be parallel to one another.

Experimental.—The sodium chloride sample was prepared by the method of Craig and McIntosh.[10] The temperature control was effected by a cryostat based on a design by J. A. Morrison.[11] The ethane was Matheson Research Grade, further purified by passing through *Ascarite* and concd. H_2SO_4 and then fractionated twice into a storage bulb.

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[7] S. Ross, THIS JOURNAL, **70**, 3830 (1948).

[8] J. R. Partington, "Advanced Treatise on Physical Chemistry," Vol. I, Longmans, Green and Co., London, 1949, p. 628.

[9] J. H. de Boer, "The Dynamical Character of Adsorption," Clarendon Press, Oxford, 1953, pp. 168–169.

[10] A. Craig and R. McIntosh, *Can. J. Chem.*, **30**, 448 (1952).

[11] J. A. Morrison, private communication.

DEPARTMENT OF CHEMISTRY
RENSSELAER POLYTECHNIC INSTITUTE
TROY, N. Y.
HADDEN CLARK
SIDNEY ROSS

RECEIVED OCTOBER 28, 1953

LONG RANGE MIGRATION OF CHEMICAL ACTIVITY IN THE SOLID STATE

Sir:

In a study of the chemical effects of the irradiation *in vacuo* of solid polyethylene in the heavy water pile of the Argonne National Laboratory, it has been found that the concentration of vinylidene groups, of which the total unsaturation of the unirradiated polyethylene is constituted—one vinylidene group per molecule—decreases linearly with time of irradiation while simultaneously the concentration of *trans*-vinylene groups increases. These results as estimated from infrared absorption studies are shown in Fig. 1.

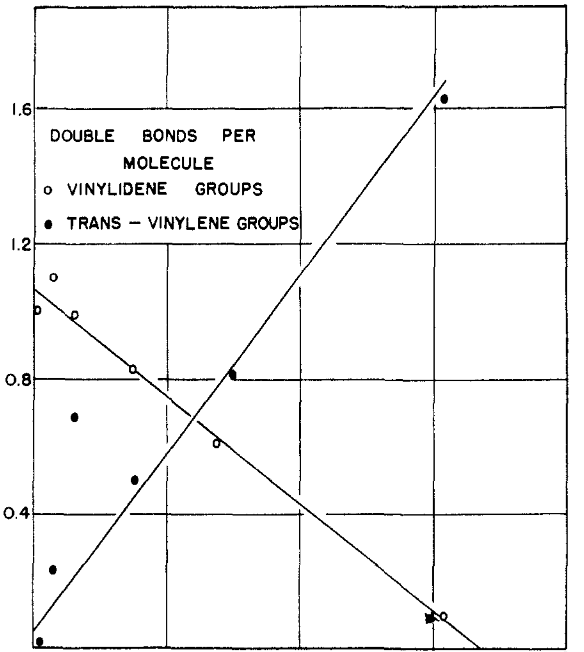

Fig. 1.

As there exists in this type of polyethylene only one vinylidene group per 2300 carbon atoms, the statistical probability of the vinylidene group being affected by the incident radiation is only two in 2300; yet the results indicate that one vinylidene group is eliminated for every 3.6 molecules of hydrogen evolved. To explain this interesting fact the hypothesis of the long range migration of chemically active centers in the polyethylene is postulated.

These chemically active centers may be either hydrogen atoms which must be produced in large numbers because of the relatively large amounts of hydrogen gas liberated, or positive or carbonium ions or free radical centers. Space does not permit a discussion as to the relative probabilities of each of these entities being the chemically active center; such discussion will be reserved for a more detailed publication. Free radicals must be produced by the abstraction by atomic hydrogen of hydrogen from the paraffinic chains of polyethylene as well as by the incident radiation or ionization produced by the irradiation; hence it is free radicals to which this discussion will be limited.

Free radicals when first formed would presumably exist for quite long periods of time as they can disappear only by reaction with other free radicals which migrate slowly through the solid polyethylene. By a "random walk" mechanism between energetically equivalent positions, the free radical centers are postulated to move along the carbon chain until localized at the vinylidene groups where an energy state estimated to be approximately 9–10 kcal./mole lower than along the hydrocarbon chain serves effectively to trap the free radical centers. These free radical centers thus activate the vinylidene groups and cause their initial rapid disappearance.

As the disappearance of the vinylidene groups follows a zero order rate law, the evidence again shows that the incident radiation is not responsible directly for this effect. The initial disappearance of the vinylidene group is also brought about by the bombardment of polyethylene with cathode rays.[1] The effect, therefore, may be a general one.

Details of this work including a description of previous work[2] on the cross-linking and unsaturation produced in polyethylene by high energy radiations, and including an application of the postulate of this note to the work of others will shortly be submitted for publication.

Grateful acknowledgment is expressed to the Visking Corporation of Chicago for financial support of this research and to the technical staff of the Argonne National Laboratory for their coöperation.

(1) Private communication from Dr. P. H. Lindenmeyer, The Visking Corporation, Chicago.

(2) D. G. Rose, M.S. Thesis, Northwestern University, 1948; M. Dole, Report of Symposium IV, "Chemistry and Physics of Radiation Dosimetry," Army Chemical Center, Maryland, 1950, p. 120.

NORTHWESTERN UNIVERSITY MALCOLM DOLE
EVANSTON, ILLINOIS C. D. KEELING

RECEIVED NOVEMBER 2, 1953

STUDIES ON POLYPEPTIDES. V. THE SYNTHESIS OF ARGININE PEPTIDES[1]

Sir:

The amino acid L-arginine is a constituent of a number of biologically active polypeptides and methods for its incorporation into peptide structures are of considerable importance.

As far as we were able to ascertain the synthesis of low molecular weight L-arginyl peptides, *i.e.*, peptides in which the carboxyl group of L-arginine is linked to the amino group of another amino acid, has hitherto not been achieved.

We wish to present the preparation of the first three representatives of this class of compounds, namely L-arginyl-L-alanine, L-arginyl-L-phenylalanine and L-arginyl-L-tyrosine.

Carbobenzoxy-L-nitroarginine[2] served as the key intermediate in our method of synthesis. Previous attempts to convert this substance into a hydrazide or acid chloride were unsuccessful.[3] We have now observed that carbobenzoxy-L-nitroarginine forms a mixed anhydride[4,5] when it is subjected to the action of ethyl chloroformate in the presence of a tertiary amine. This mixed anhydride reacts with amines and amino acid or peptide esters to give the respective carbobenzoxy-L-nitroarginyl amides and peptide esters. In this manner carbobenzoxy-L-nitroarginine was combined with aniline to give carbobenzoxy-L-nitroarginyl anilide, m.p. 167–168°, $[\alpha]^{27}\text{D}$ −3.5° (in CH_3OH). *Anal.* Calcd. for $C_{20}H_{24}O_5N_6$: C, 56.1; H, 5.6; N, 19.6. Found: C, 56.2; H, 5.5; N, 19.7. The interaction of the mixed anhydride with the methyl esters of L-alanine, L-phenylalanine and L-tyrosine gave: (1) carbobenzoxy-L-nitroarginyl-L-alanine methyl ester, m.p. 155–157°, $[\alpha]^{25}\text{D}$ −18.8° (in CH_3OH). *Anal.* Calcd. for $C_{18}H_{26}O_7N_6$: C, 49.3; H, 6.0; N, 19.2. Found: C, 49.5; H, 5.9; N, 19.3; (2) carbobenzoxy-L-nitroarginyl-L-phenylalanine methyl ester, m.p. 131–132°, $[\alpha]^{25}\text{D}$ −8.2° (in CH_3OH). *Anal.* Calcd. for $C_{24}H_{30}O_7N_6$: C, 56.0; H, 5.9; N, 16.3. Found: C, 55.7; H, 5.7; N, 16.1; (3) carbobenzoxy-L-nitroarginyl-L-tyrosine methyl ester, m.p. 159–160°, $[\alpha]^{25}\text{D}$ −3.5° (in CH_3OH). *Anal.* Calcd. for $C_{24}H_{30}O_8N_6$: C, 54.3; H, 5.7; N, 15.8. Found: C, 54.2; H, 5.4; N, 15.9.

Saponification with aqueous sodium hydroxide converted these peptide esters into the corresponding carbobenzoxy-L-nitroarginyl peptides, *i.e.*, carbobenzoxy-L-nitroarginyl-L-alanine, m.p. 207–208°, $[\alpha]^{26}\text{D}$ −11.6° (in CH_3OH), carbobenzoxy-L-nitroarginyl-L-phenylalanine, m.p. 225–226°, $[\alpha]^{26}\text{D}$ +1.6° (in CH_3OH) and carbobenzoxy-L-nitroarginyl-L-tyrosine, m.p. 164–166°, $[\alpha]^{28}\text{D}$ +8.3° (in CH_3OH).

Hydrogenation of the carbobenzoxy-L-nitroarginyl peptides in the presence of spongy palladium in methanol containing 10% by weight of glacial acetic acid gave the crystalline diacetate salts of the respective L-arginyl peptides, namely: (1) L-arginyl-L-alanine diacetate, m.p. 173–174°, $[\alpha]^{27}\text{D}$ +12.2° (in H_2O). *Anal.* Calcd. for $C_{13}H_{27}O_7N_5$: C, 42.7; H, 7.4; N, 19.2. Found: C, 42.9; H, 7.4; N, 19.4; (2) L-arginyl-L-phenylalanine diacetate, m.p. 172–173°, $[\alpha]^{28}\text{D}$ +23.9° (in H_2O). *Anal.* Calcd. for $C_{19}H_{31}O_7N_5$: C, 51.7; H, 7.1; N, 15.9. Found: C, 52.4; H, 7.0; N, 16.1; (3) L-arginyl-L-tyrosine diacetate, m.p. 157–158°, $[\alpha]^{27}\text{D}$ +30.4° (in H_2O). *Anal.* Calcd. for $C_{19}H_{31}O_8N_5$: C, 49.9; H, 6.8; N, 15.3. Found: C, 49.6; H, 7.2; N, 15.1. The salts exhibited a positive Sakaguchi test, gave a blue color with ninhydrin, and contained no detectable quantities of ammonium acetate.

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[1] The authors wish to express their appreciation to Armour and Company and to the U.S. Public Health Service for their generous support of this investigation.

(2) M. Bergmann, L. Zervas and H. Rinke, *Z. physiol. Chem.*, **224**, 40 (1934).

(3) J. S. Fruton, "Advances in Protein Chemistry," Vol. V, Academic Press, Inc., New York, N. Y., 1949, p. 64.

(4) T. Wieland and R. Sehring, *Ann.*, **569**, 122 (1950).

(5) R. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951).

A detailed description of our synthetic methods and their application to the synthesis of other L-arginyl peptides will be presented at a later date.

BIOCHEMISTRY DEPARTMENT, UNIVERSITY OF PITTSBURGH SCHOOL OF MEDICINE
PITTSBURGH, PENNSYLVANIA
KLAUS HOFMANN
ALFRED RHEINER
WILLIAM D. PECKHAM

RECEIVED SEPTEMBER 8, 1953

THE BIOSYNTHESIS OF SUCROSE[1]

Sir:

A previous note[2] reported the formation of trehalose phosphate from UDPG[3] and glucose-6-phosphate. Following the same general procedure, an enzyme has now been found in wheat germ which catalyzes the reaction UDPG + fructose ⇄ sucrose + UDP. The evidence is as follows. The product formed was found to be non-reducing and to behave like sucrose on paper chromatography with two solvents (butanol–acetic acid[4] and ethyl acetate–pyridine[5]). After extraction of the substance from the paper followed by hydrolysis with dilute acid (5 minutes at *p*H 2 at 100°) or with purified invertase, glucose and fructose were detected chromatographically.

As shown in Table I, equal amounts of sucrose and UDP are formed in the reaction. The disappearance of UDPG and the formation of UDP were checked semiquantitatively after separation by paper chromatography with ethanol–ammonium acetate–Versene[6] as solvent.

TABLE I

The complete system contained 0.05 μmole of UDPG, 2 μmoles of fructose and 0.05 ml. of enzyme,[a] 0.1 ml. of 0.1 *M* sodium diethyl barbiturate: final volume, 0.25 ml.; *p*H 8.6; incubated during 10 minutes at 37°. The Δ values represent the difference in μmoles with a non-incubated sample.

	Δ Sucrose[b]	Δ UDP[c]	Δ Inorganic phosphate
Complete system	0.33	0.30	0.05
No UDPG	0	0	0
No fructose	0	0.05	0.04

[a] The enzyme was obtained by extracting wheat germ with three volumes of phosphate buffer 0.05 *M*, *p*H 7. After centrifuging the supernatant was dialyzed overnight cold and centrifuged again. The supernatant was precipitated twice by adding 35 g. of ammonium sulfate per 100 ml. The precipitate was suspended in water, dialyzed for 2 hours and adjusted to *p*H 5. The precipitate was redissolved in water at *p*H 7. The precipitation with acid was repeated three times. The solution contained 40 mg. of protein per ml. [b] Sucrose was estimated by the resorcinol method[7] after destroying the fructose by heating 10 minutes at 100° in 0.01 *N* NaOH. [c] Determined enzymatically.[2]

The same chromatographic procedure was used for studying the reversibility. Starting with UDP and sucrose it was found that UDPG is formed. Its identity was checked by extracting it from the paper and measuring the coenzymic activity on galactowaldenase.[8] The data indicate that the equilibrium is displaced in favor of sucrose synthesis.

No sucrose formation or UDPG disappearance was found to occur if glucose-1-phosphate was added instead of UDPG, or if sorbose, aldoses, arabinose or the 1- or 6-phosphates of fructose or glucose were substituted for fructose.

Although sucrose had been previously obtained by enzymic action, the mechanism of the synthesis in plants remained obscure. The enzyme which Doudoroff and Hassid extracted from *Pseudomonas saccharophyla* catalyzes the formation of sucrose from glucose-1-phosphate and fructose, but it has not been possible to detect such a reaction in plant material.[9] The enzyme described in this paper has been found to be present not only in wheat germ but also in corn and bean germs and in potato sprouts. Tests for UDPG by its coenzymic activity gave positive results on wheat germ extracts.

Moreover, Buchanan, *et al.*[10] have published evidence of the presence of UDPG in other plants. They also suggested that it was involved in sucrose synthesis, probably by reacting with fructose phosphate to give sucrose phosphate. The latter substance can be excluded as an intermediate in the reaction catalyzed by the wheat germ enzyme because the product is all free sucrose and only negligible amounts of inorganic phosphate are released (Table I).

(1) This investigation was supported in part by a research grant (G-3442) from the National Institutes of Health, United States Public Health Service, and by the Rockefeller Foundation.

(2) L. F. Leloir and E. Cabib, THIS JOURNAL, **75**, 5445 (1953).

(3) The abbreviations UDPG for uridine diphosphate glucose, and UDP for uridine diphosphate are used.

(4) S. M. Partridge, *Biochem. J.*, **42**, 238 (1948).

(5) M. A. Jermyn and F, A. Isherwood, *Biochem. J.*, **44**, 402 (1949).

(6) E. Cabib and L. F. Leloir, *J. Biol. Chem.*, in press.

(7) J. H. Roe, *J. Biol. Chem.*, **107**, 15 (1934).

(8) R. Caputto, L. F. Leloir, C. E. Cardini and A. C. Paladini, *J. Biol. Chem.*, **184**, 333 (1950).

(9) W. Z. Hassid, "A Symposium on Phosphorus Metabolism," The Johns Hopkins Press, Baltimore, Md., 1951, p. 11.

(10) (a) J. G. Buchanan, *Arch. Biochem. and Biophys.*, **44**, 140 (1953); (b) J. G. Buchanan, V. H. Lynch, A. A. Benson, D. F. Bradley, and M. Calvin, *J. Biol. Chem.*, **203**, 935 (1953).

INSTITUTO DE INVESTIGACIONES BIOQUÍMICAS
FUNDACIÓN CAMPOMAR, J. ALVAREZ 1719
BUENOS AIRES, ARGENTINA
L. F. LELOIR
C. E. CARDINI

RECEIVED 4, 1953

CONFIGURATIONS OF LIGANDS HAVING INTERNAL ROTATION AXES IN COÖRDINATION COMPOUNDS

Sir:

Considerable evidence based on spectroscopic, thermal and electric measurements has been accumulated to indicate that 1,2-disubstituted ethanes, $XH_2C–CH_2X$, exist in *trans* and *gauche* configurations in the gaseous and liquid states and in solutions, but they exist only in *trans* configuration in the solid state.[1] Our infrared measurements on ethylene thiocyanate have also shown that this substance exists in the *trans* and *gauche* configurations in chloroform solutions but it exists only in *trans* configuration in the solid state. The spectrum of the complex $[PtCl_2(CH_2SCN)_2]$ has been found to be quite similar to that of the *gauche* configuration of ethylene thiocyanate but quite different from that of the *trans* configuration. Therefore, the configuration of this chelate ligand in the co-

(1) S. Mizushima, Y. Morino, I. Watanabe, T. Shimanouchi and S. Yamaguchi, *J. Chem. Phys.*, **17**, 591 (1949); S. Mizushima, T. Shimanouchi, I. Nakagawa and A. Miyake, *J. Chem. Phys.*, **21**, 215 (1953); see also S. Mizushima, "The Reilly Lectures," Vol. 5, The University Press of Notre Dame, Notre Dame, Indiana, 1951.

ordination complex can be concluded to be *gauche*. The fact that the C≡N frequency of ethylene thiocyanate is not appreciably changed in the complex indicates that coördination takes place through the sulfur atom; furthermore the complex shows the usual color and chemical properties characteristic of Pt–S coördination compounds.

A similar conclusion was drawn from our infrared measurements for the configuration of ethylenediamine when this molecule is present as a chelating group in coördination complexes. The bond lengths in coördination complexes can best be explained on the basis of the *gauche* configuration of this chelating group and this configuration is in agreement with the results of the X-ray investigations.[2,3] The *cis* configuration has so far been tacitly assumed for the ethylenediamine ligand in these coördination compounds.

The conclusion of the *gauche* configurations is of interest to the stereochemistry of these complexes, for the *gauche* configuration has a mirror image non-superposable. Thus more optical isomers are theoretically possible if the chelating group present in these complexes has the *gauche* rather than the *cis* configuration.[4] For example, in *cis*-[Co(H_2-NH_2C–$CH_2NH_2)_2Cl_2$]Cl there are more optical isomers than would be expected from the classical viewpoint. In the case of the corresponding *trans* isomer, however, only one configuration is present since our infrared analysis as well as the X-ray investigation[3] have shown that the two ethylenediammine ligands in the coördination complex are present as two configurations which are the mirror images of each other.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
J. V. QUAGLIANO[5]
SAN-ICHIRO MIZUSHIMA

RECEIVED SEPTEMBER 3, 1953

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[2] T. Watanabe and M. Atoji, *Kagaku* (*Science*), **21**, 301 (1951).

[3] A. Nakahara, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, **25**, 331 (1952).

[4] M. Kobayashi, *J. Chem. Soc. Japan*, **64**, 648 (1943).

[5] Member, Radiation Project operated by the University of Notre Dame and supported in part under AEC Contract AT(11-1)-38.

THE PARTIAL AMMONOLYSIS OF SILICON TETRACHLORIDE

Sir:

It has been pointed out in earlier work[1] that the partial hydrolysis of silicon halides, carried out under conditions such that complete conversion into silica and hydrochloric acid is not effected, leads to the formation of mixtures containing oxyhalides of silicon, homologous series of which have been isolated by careful fractionation of the reaction products.

It seemed of interest to determine whether partial ammonolysis of such halides might be accomplished, leading, for example, to imino-halides, such as $Si_2(NH)Cl_6$, from the partial ammonolysis of $SiCl_4$.

Preliminary experiments in which ammonia gas, diluted with nitrogen, was passed into an ethereal solution of silicon tetrachloride at −75°, or over the surface of an ethereal solution of silicon tetrachloride at 0°, or over the surface of pure silicon tetrachloride at −70°, yielded only solid, highly polymerized materials of undetermined composition. Similar unsatisfactory results were obtained when an ether solution of silicon tetrachloride was allowed to react with silver chloride triamine, $AgCl \cdot 3NH_3$, as the ammoniating agent.

However, when the vapors of silicon tetrachloride were allowed to react with ammonia, diluted with dry nitrogen, at 825° for thirty-five hours, there were isolated besides solid polymerized materials, two compounds of the silazane type. The first of these, a colorless liquid boiling at 34° under 3 mm. pressure, and freezing about −50°, was identified by analysis and molecular weight determinations as the iminochloride, $Si_2(NH)Cl_6$. The second substance, a colorless, crystalline solid at room temperature, boiling at 103° at 2 mm. pressure and melting at about 50°, corresponded similarly to the formula $Si_8N_4Cl_{20}$, a cyclic tetramer, or possibly to $Si_9N_5H_2Cl_{23}$, an open-chain structure. The alkyl analogs of the first compound, hexamethyldisilazane and hexaethyldisilazane, Me_6Si_2NH and Et_6Si_2NH, were reported by Sauer, *et al.*[2]

It is reasonable to suppose that hexachlorodisilazane represents the first member of a homologous series of straight-chain compounds of the general formula, $Sn_n(NH)_{n-1}Cl_{2n-2}$.

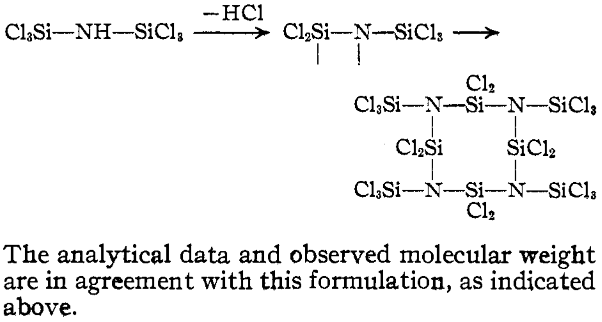
Anal. Si: calcd., 19.77; found, 19.90, 19.48, 19.60; av., 19.66. Cl: calcd., 74.94; found, 76.04, 75.60, 75.94; av., 75.86. N: calcd., 4.94; found, 4.85, 4.91, 5.05; av., 4.94. Mol. wt., for $Si_2(NH)Cl_6$: calcd., 283.9; found, 293, 275; av., 284.

Analysis of the second, crystalline compound gave the following results:

	Calcd. for $Si_8N_4Cl_{20}$	Calcd. for $Si_9N_5Cl_{23}$	Found	Av.
Si:	22.68	22.15	22.60, 22.47	22.53
Cl:	71.66	71.53	71.66, 71.86, 71.69	71.74
N:	5.66	6.14	5.90, 6.18, 6.24	6.11

Mol. wt., calcd. for $Si_8N_4Cl_{20}$, 990; for $Si_9N_5H_2Cl_{23}$, 1140; found, 1178, 1060; av., 1119.

This crystalline solid substance could be considered as derived from hexachlorodisilazane by the elimination of HCl and the formation of a cyclic tetramer



The analytical data and observed molecular weight are in agreement with this formulation, as indicated above.

Alternatively, if condensation of three moles of $Si_2(NH)Cl_6$ with one of the second member of the series, $Si_3(NH)_2Cl_8$, occurred, with splitting out of

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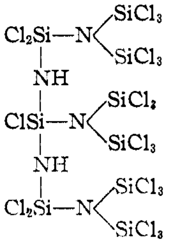
[1] W. C. Schumb and A. J. Stevens, THIS JOURNAL, **69**, 726 (1947); **72**, 3178 (1950); W. C. Schumb and R. A. Lefever, *ibid.*, **75**, 1513 (1953).

[2] R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944); R. O. Sauer and R. H. Hasek, *ibid.*, **68**, 241 (1946).

HCl, the following chain structure, corresponding with $\mathrm{Si_9N_5H_2Cl_3}$, would result



The agreement here with the analytical results is substantially as good as that given by the first structure, and the molecular weight found is somewhat closer to the calculated value in this case.

The analysis of the solid polymeric residue left after heating the solid reaction products under reduced pressure, to sublime away any ammonium chloride, while not as conclusive as that presented for the silazanes, led to results approaching the requirements of the simple empirical formula, $(\mathrm{Cl{-}Si{\equiv}N})_x$. One such sample, for example, gave the following data:

Si: 36.5, 35.9; av. 36.3; g.-atoms, 1.1
Cl: 40.9, 40.5; av. 40.7; g.-atoms, 1.0
N: 18.6, 19.4; av. 19.0; g.-atoms, 1.2

Under the conditions of sublimation *in vacuo* any entrapped ammonium chloride would be expected to have been removed; nevertheless, X-ray film of samples thus treated invariably showed lines due to ammonium chloride, which is believed to have resulted from hydrolysis of the sample due to contact with moisture of the air. It is thought, therefore, that the solid is not merely a mixture of either $\mathrm{Si(NH)_2}$ or $\mathrm{Si(NH_2)_2NH}$, reported by Stock,[3] with ammonium chloride, but rather that it consists essentially of the polymerized chloronitride, $(\mathrm{Cl{-}SiN})_x$.

Further studies on the ammonolytic and hydrolytic characteristics of the halides and oxyhalides of silicon, which have been in progress for the past few years, will be presented shortly in a definitive paper.

[3] A. Stock and F. Zeidler, *Ber.*, **56**, 986 (1923).

DEPARTMENT OF CHEMISTRY WALTER C. SCHUMB
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASS. LELAND H. TOWLE

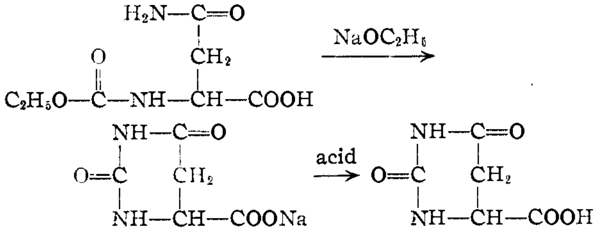
RECEIVED SEPTEMBER 30, 1953

DIHYDROÖROTIC ACID

Sir:

Bachtez and Cavallini[1] have reported a synthesis of "dihydroörotic acid" by fusion of maleic acid and urea. Workers in this laboratory[2] have reported that "dihydroörotic acid" prepared by this method was not active in supporting growth of *Lactobacillus bulgaricus 09* which responds to either ureidosuccinic acid or orotic acid. Recently, Kornberg and co-workers[3] discovered an enzyme system which reversibly converts orotic acid to dihydroörotic acid but which would not utilize "dihydroörotic acid" prepared by the method of Bachtez and Cavallini.

While seeking an answer to this discrepancy, a new synthesis of dihydroörotic acid was devised. D- L- or DL-N$^\alpha$-carbethoxyasparagine was heated under reflux for four hours in an ethanol solution containing 2 molar equivalents of sodium ethoxide to give the corresponding D-, L- or DL-dihydroörotic acid in yields up to 70%. The use of sodium methoxide in methanol gave erratic results.



Heating of dihydroörotic acid with strong mineral acid converts it into 5-hydantoinacetic acid. This reaction apparently goes via ureidosuccinic acid since use of too much acid in the isolation of DL-dihydroörotic acid results in a product contaminated with DL-ureidosuccinic acid.

L-Dihydroörotic acid obtained from N$^\alpha$-carbethoxy-L-asparagine had the properties: decomposed at 266°; $[\alpha]^{25.3}\mathrm{D}$ $+33.23°$ (*c* 1.992)[4] in 1% $\mathrm{NaHCO_3}$. *Anal.* Calcd. for $\mathrm{C_5H_6O_4N_2}$: C, 37.98; H, 3.83; N, 17.72. Found: C, 38.18; H, 3.97; N, 17.69.[5]

D-Dihydroörotic acid obtained from N$^\alpha$-carbethoxy-D-asparagine had the properties: decomposed at 266°; $[\alpha]^{25.3}\mathrm{D}$ $-31.54°$ (*c* 2.01) in 1% $\mathrm{NaHCO_3}$. *Anal.* Found: C, 37.69; H, 4.03; N, 17.71. A sample of this material was converted to the brucine salt which was recrystallized to constant decomposition point (268°) and constant optical rotation [$[\alpha]^{25}\mathrm{D}$ $-32.15°$ (*c* 1.039) in water]. The brucine salt was decomposed with acid and the dihydroörotic acid obtained freed from brucine by repeated recrystallization from water. Its properties were $[\alpha]^{26.5}\mathrm{D}$ $-34.29°$ (*c* 2.488) in 2.5% $\mathrm{NaHCO_3}$ and decomposition at 267–268°.

DL-Dihydroörotic acid obtained from N$^\alpha$-carbethoxy-DL-asparagine decomposed at 259° and was optically inactive. *Anal.* Found: C, 38.23; H, 3.85; N, 17.67.

DL-Dihydroörotic acid prepared from N$^\alpha$-carbethoxy-DL-asparagine has been found to differ in melting point, infrared spectrum and solubility with material prepared by the method of Bachtez and Cavallini. An attempt to resolve the material prepared by the method of Bachtez and Cavallini into D and L isomers by recrystallization of its brucine salt was unsuccessful.

Microbiological tests carried out in these labora-

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[1] M. Bachtez and G. Cavallini, *Ber.*, **66B**, 681 (1933).

[2] D. S. Spicer, K. V. Liebert, L. D. Wright and J. W. Huff, *Proc. Soc. Exptl. Biol. Med.*, **79**, 587 (1952).

[3] J. Lieberman and A. Kornberg, *Federation Proc.*, **12**, 239 (1953).

[4] We are indebted to H. C. Zell for the optical measurements.

[5] We are indebted to Joyce Pyett, Arthur Fadenrecht and Kermit B. Streeter for the microanalyses.

tories with *Lactobacillus bulgaricus 09*[6] have shown that L-dihydroörotic acid and DL-dihydroörotic acid prepared by the new procedure will support growth and that the activity of these substances as well as of orotic acid and ureidosuccinic acid are reversibly inhibited by D-dihydroörotic acid.

DEPARTMENT OF ORGANIC CHEMISTRY
SHARP AND DOHME DIVISION
MERCK AND CO., INC.
WEST POINT, PA.

CHARLES S. MILLER
JANICE T. GORDON
EDWARD L. ENGELHARDT

RECEIVED OCTOBER 26, 1953

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[6] L. D. Wright, C. A. Driscoll, C. S. Miller and H. R. Skeggs, *Proc. Soc. Exptl. Biol. Med.*, in press.

BOOK REVIEWS

Radiocarbon Dating. By WILLARD F. LIBBY, Professor of Chemistry, Institute of Nuclear Studies, University of Chicago. The University of Chicago Press, Chicago 37, Illinois. 1952. vii + 124 pp. 16 × 24 cm. Price, $3.50.

An undergraduate elective course gave this reviewer a side interest in geology and the seemingly unanswerable question: "How long has geology been a-making?" Five years later as a doctorate candidate in analytical chemistry he was exposed to a geochemical infection by contact with the late Alfred C. Lane, and helped to date several uranium-containing specimens. The uranium–thorium–lead method put reliable dates into the range of historical geology down to the most recent 100 million years; of this remaining recent void, the last 20,000 holds much of the interest, and now Professor Libby's group has made possible the radiocarbon dating of pre- and post-ice age materials. Hess' discovery of cosmic radiation in 1911 meant little to the nuclear chemist of those days, but the discovery of the neutron, its production by cosmic ray action in the atmosphere, and the reaction $N^{14} + n = H^1 + C^{14}$ all combined to give us radiocarbon dating, the C^{14} half-life of 5568 ± 30 years setting a practical limit of about 20,000 years, and with thanks to the long-gone plants which fixed the radioactive carbon dioxide and the animals which helped the plants to preserve it for use by Libby's testers.

In Chapter I the author presents the nuclear background, which is more complex than indicated above, and carefully cites and evaluates the many pertinent variables: the long-period constancy of cosmic radiation, the earth's radiocarbon inventory, its cycle of distribution and utilization, and the problem of reliable choice of reliable specimens. Chapter II continues the study, bringing up the question of the vertical and horizontal variations of neutron intensity, rate of exchange between atmospheric and fixed carbon dioxide (in ocean and land compounds), the mixing of the ocean reservoir, and the constancy of cosmic radiation during recent millennia. Chapter III deals with the method of arriving at the half-life value of carbon-14.

With the background theory and experiment covered, Chapter IV considers the preparation of the sample for measurement, with its problems of inorganic and organic combination, alteration of original substances by putrefaction, heat and possible exchange. Acceptable sample materials are charcoal, wood, grasses, peat, antlers and hairy materials, and shell. More or less thoughtfully planned and executed preparation is needed before any sample (in amount to yield 12 to 5 g. of final carbon) is ready for combustion to carbon dioxide, processing of the gas and reduction of the gas to carbon by hot magnesium. This carbon product requires further treatment to give the final carbon powder, which even yet contains some 10% of ash as magnesium oxide.

Chapter V describes the measurement of the radioactivity of the carbon, by an apparatus using a modified Geiger counter, and includes considerable discussion of apparatus and operational details which might have effects on the answers. For measurement the carbon powder is made into a mush which is spread thinly and evenly on the inside of the measuring cylinder; the water is dried out with pumping to the micron range, and an atmosphere of poorly adsorbed ethylene and argon is introduced. The cylinder is now ready for measurement. in an apparatus in which it is surrounded by a screen-wall of plain Geiger counters to reduce the activity background. The actual measuring run-time is 48 hours, with further time for background determinations.

Chapter VI lists materials measured and dates assigned for work done prior to late 1951, a total of 218 different samples. The specimens are from all parts of the globe, and represent relics of "literate" and illiterate recent and early man, of plant life related to pre- and post-glacial periods, of logs buried in the sands of time, and ancient vegetation gone to sodden peat in arctic and temperate climes. The ages found vary from a juvenile 712 ± 200 to the ancient "at least 21,000" years. The whole list is a wonderful help and factual spiritual lift to the time-counting archeologist, geologist and palynologist, as Frederick Johnson makes clear in Chapter VII. These last fifteen pages serve to interrelate the radiocarbon datings with previous chronology, showing how many perplexities are resolved, even though some remain and a few new ones are created. Just as uranium-lead ratios showed that thus measurable geologic time began some 2,000,000,000 years ago, that the Cambrian period went back 850,000,000 years and the youngest rocks with measurable ratios are maybe 100,000,000 years old, so now we know that Folsom man made arrow points 10,000 years past, the Mankato glacial period dates only 11,000 instead of 25,000 years back, it is 6500 years since Mt. Mazama blew its crown to dust to give us bottomless Crater Lake, and some nameless aborigines trapped fish 5700 years ago on Boylston Street, Boston.

It is only a little book but good things often come in small packages, and this one is good reading for all sorts of ordinary non-nuclear chemists.

DEPARTMENT OF CHEMISTRY
SIMMONS COLLEGE
BOSTON 15, MASS.

ALLEN D. BLISS

Chemistry and Methods of Enzymes. Third Edition. By JAMES B. SUMNER, Professor of Biochemistry, Cornell University, and G. FRED SOMERS, Chairman, Dept. of Agricultural Chemistry and Associate Director, Agricultural Experiment Station, University of Delaware. Academic Press, Inc., 125 East 23rd Street, New York 10, N. Y. 1953. xvi + 462 pp. 16.5 × 23.5 cm. Price, $7.50.

In this, the 3rd edition, out 5 years after the 2nd, the authors have added new and dropped old material keeping the size of the book fairly unchanged. Since Sumner crystallized the first enzyme, urease, in 1926, a large number of enzymes from animal and plant tissues, from bacteria and molds have been crystallized and all proved to be proteins. In fact, the authors turn the sentence around and state that probably most proteins are enzymes. Enzyme chemistry has become a part of protein chemistry, in which determination of specific activity provides a particularly sensitive method for determination of purity and native state of the protein. The methods of purification still depend largely on art, with few generally applicable rules. Throughout the book one finds observations and remarks testifying to the long laboratory experience of the authors. This gives the