I. Introduction

Subsequent to Strecker's observation (49) that alloxan reacts with alanine to give carbon dioxide and acetaldehyde, a number of reagents have been found having the power of producing such changes. No review has appeared covering this field, though the importance of this degradation—*inter alia*, for biological and analytical processes—has been established for a long time.

In honor of Strecker, the term "Strecker degradation" has recently been proposed (46) for the degradation of α-amino acids by carbonyl compounds, but it seems advisable to use this term for all degradations of α-amino acids to aldehydes and ketones containing one carbon atom less, whatever the degrading agent may be; in this sense, the term "Strecker degradation" (or simply "degradation") is used in this review.

The Strecker degradation may be grouped under the headings of catalytic and noncatalytic processes, the latter being the more important. Agents (tables 1 and 2) which bring about the noncatalytic degradation may be divided into inorganic or organic or into (*a*) those which degrade α-amino acids with unsubstituted amino groups only, e.g., ninhydrin (46), and (*b*) those which are also active when the amino group is substituted, e.g., *N*-chloro-*p*-toluenesulfonamide, which degrades *N*-methylaminophenylacetic acid to benzaldehyde (9).

The various agents which have been used are summarized in table 1. The reactions were carried out in an aqueous medium (water, water–glycerol, water–pyridine, water–acetic acid) at atmospheric pressure and at temperatures ranging from ordinary room temperature to the boiling point of the solvent mixture.

It should be noted that Strecker degradations effected by light or *in vivo* are outside the scope of this review.

TABLE 1

Agents used in the Strecker degradation of amino acids

AGENTS	SECTION
Inorganic agents:	
Ozone, hydrogen peroxide, silver oxide, persulfates, oxygen (anodic oxidation)	II
Organic agents:	
Ketones and aldehydes	III, A
Per acids and derivatives: e.g., perbenzoic acid and benzoyl peroxide	III, C
N-Chloroarylsulfonates, *N*-bromosuccinimide, and analogs	III, C
Derivatives and analogs of triphenylcarbinol, e.g., malachite green	III, C
Catalytic degradations: oxygen in the presence of a catalyst	IV

II. Strecker Degradations Effected by Inorganic Agents

Ozone: Bergel and Boltz (6) have degraded α-amino acids (in water) by the action of ozone; degradation was effected not only with amino acids having a free amino group (e.g., leucine) but also with α-amino acids without such a group, e.g., α-(*N*,*N*-dimethylamino)isobutyric acid. The following equation has been suggested:

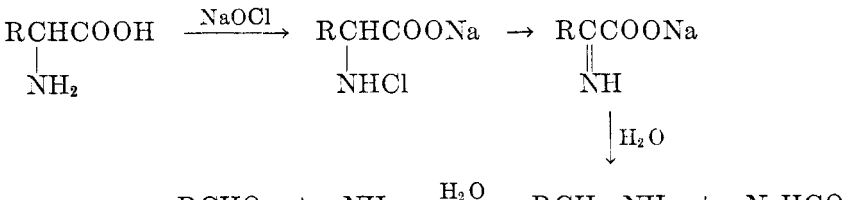
$$RCH(NH_2)COOH + O_3 + O_2 + H_2O \rightarrow RCHO + CO_2 + NH_3 + H_2O_2 + O_2$$

Hydrogen peroxide: Hydrogen peroxide in the presence of ferrous sulfate degrades α-amino acids at ordinary temperature; thus, glycine yielded formaldehyde (8). Oxidation by the action of hydrogen peroxide in acidic medium in the presence of ferrous sulfate gave similar results; thus, alanine with 30 per cent hydrogen peroxide yielded acetaldehyde (10).

Silver oxide: Herbst and Clarke (11) investigated the action of silver oxide on α-amino acids in hot aqueous solutions; the products were ammonia (or the

corresponding amines), carbon dioxide, and aldehydes which were partly oxidized to the corresponding acids. α-Amino acids having either a free or a substituted amino group reacted; thus, α-aminophenylacetic acid yielded benzaldehyde and benzoic acid in addition to carbon dioxide and ammonia; in the case of α-(*N*,*N*-dimethylamino)isobutyric acid, acetone and dimethylamine were formed. Elementary silver was also formed in these reactions.

Sodium hypochlorite: The degrading action of this reagent was studied by Langheld (23), who allowed the salt to react on α-amino acids in the presence of alkali.



Persulfate: Lang (20) carried out the reaction by allowing boiling persulfate solutions to act on α-amino acids in the presence of alkali.

Oxygen (anodic oxidation): Degradations have also been effected by electrochemical oxidation (10); thus, leucine yielded isovaleraldehyde, carbon dioxide, and ammonia.

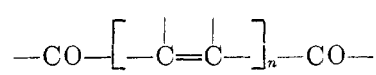
III. Strecker Degradations Effected by Organic Agents

A. Degradations effected by ketones and aldehydes

1. Degradations effected by ketones

Schönberg, Moubacher, and Mostafa (46) have investigated the degrading power of a large number of ketones. The experiments were performed in water or in a water–glycerol mixture, in an atmosphere of carbon dioxide or nitrogen, and in the absence of salts, bases, or acids, with the exception of carbonic acid. The addition of glycerol served to facilitate the wetting of the carbonyl compounds or to increase their solubility.

Ketones were found to be active, provided they contained the following grouping, where $n = 0$ or an integer (compare tables 2 and 3):



Ia

The double bond of this grouping may be of an aromatic character (*cf.* anthraquinone); nevertheless, not all substances containing this group effect the degradation, e.g., *s*-dibenzoylethylene (46). The reason for this is that, when treated with primary amines under the conditions described previously, these and related substances do not form Schiff compounds, the formation of which is the first and essential step in the Strecker degradation.

Table 2 lists α-keto acids, α-keto lactones, α-keto aldehydes, 1,2-diketones, *o*- and *p*-quinones and related compounds which cause the Strecker degradation

TABLE 2

Ketones found to be active in the Strecker degradation of α-amino acids (46)

Group A. Ketones which contain the group shown in formula Ia, n being equal to zero:	Oxalyl dibenzyl ketone (VII)
Pyruvic acid	Retenequinone
Biacetyl	Bis-1,3-diketoindoxylidene (VIII) (41)
Alloxan (XVI)	4,4′-Bisdimethylaminobenzil
Dehydroascorbic acid	Di(ω-phenylbutadienyl) diketone (IX)
Dimethylalloxan	*o*-Benzoquinones are believed to be intermediate compounds formed during the action of catechol and derivatives on α-amino acids in the presence of oxygen
Coumarandione (I)	
Thiocoumarandione (II)	
Isatin	
Phenylglyoxal	*Group B. Ketones which contain the group shown in formula Ia, n being equal to 1:*
Phenylglyoxylic acid	Benzoquinone
Triketoindan (III)	Toluquinone
Phenylpyruvic acid	Anthraquinone
Camphorquinone	2-Methyl-1,4-naphthoquinone
Acenaphthenequinone	Thioindigo
β-Naphthacoumarandione (IV)	Indigo
peri-Naphthindantrione (V)	Vitamin K (48)
Phenanthraquinone	
Benzil	
Diphenyl triketone	*Group C. Ketones which contain the group shown in formula Ia, n being equal to 3:*
2-Hydroxy-2′-methoxybenzil	Coerulignone (X)
Aceanthraquinone (VI)	

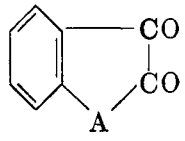
TABLE 3

Compounds which have been found to be ineffective in the Strecker degradation (46)

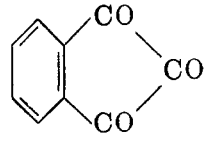
Group D. Carbonyl compounds:	Benzylideneacetophenone
Urea	Dibenzoylmethane
Oxamide	Dibenzoylethylene
Parabanic acid	Dibenzylideneacetone
p-Nitroacetophenone (44)	α-Naphthaflavone (XI)
Coumarin	Dibenzoylstilbene
Phorone	
Camphor	*Group E. Other compounds:*
Fluorenone	Azobenzene
Xanthone	*p*-Nitrosodimethylaniline (44)
Benzophenone	Methylene blue
Benzoin	Acriflavine (44)

to proceed at such a rate that it is at least 25 per cent complete in 30 min. at 100°C.

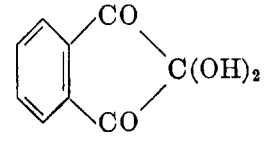
Amino acids which have been degraded (1, 34, 47) by some of the ketones mentioned in table 2 are glycine, alanine, leucine, valine, isoleucine, norvaline, norleucine, phenylalanine, glutamic acid, and α-aminoisobutyric acid.



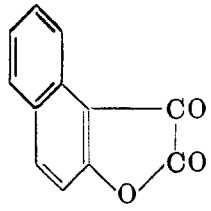
I: Coumarandione (A = O)
II: Thiocoumaradione (A = S)



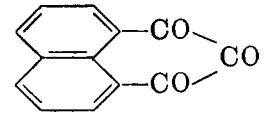
III
Triketoindan



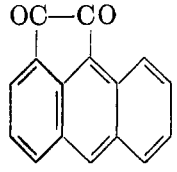
IIIa
Ninhydrin



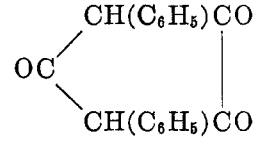
IV
β-Naphtha-coumarandione



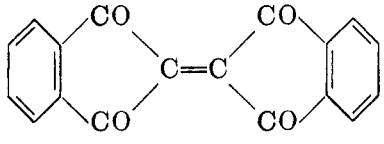
V
peri-Naphthindantrione



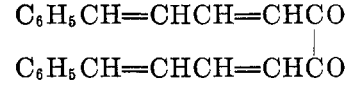
VI
Aceanthraquinone



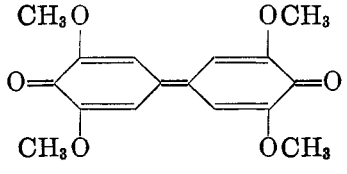
VII
Oxalyl dibenzyl ketone



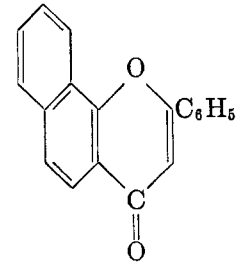
VIII
Bis-1,3-diketoindoxylidene



IX
Di(ω-phenylbutadienyl) diketone



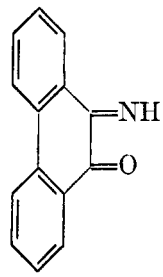
X
Coerulignone



XI
α-Naphthaflavone

2. Degradations effected by nitrogen analogs of o- and p-quinones

Phenanthraquinonimine (27) (XII) and indophenol degrade α-amino acids

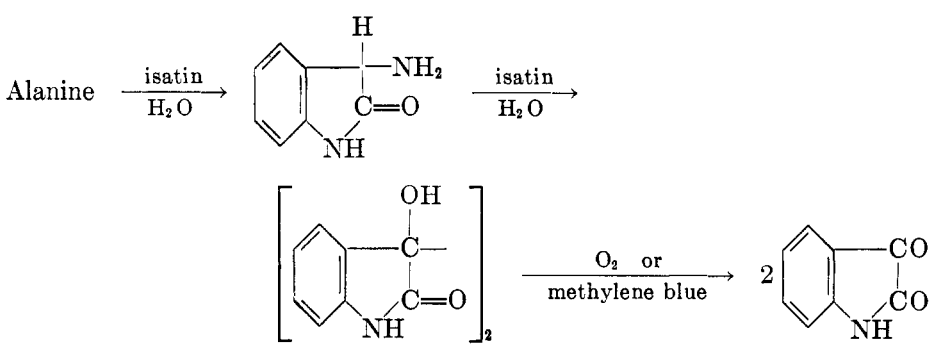


XII
Phenanthraquinonimine

in boiling water, but it is doubtful whether they degrade as such or after hydrolysis; e.g., phenanthraquinonimine is very easily hydrolyzed to phenanthrenequinone, and it is possible that the observed degrading power is actually due to the formation of phenanthrenequinone.

3. Degradation of amino acids by the action of isatin in the presence of oxygen or methylene blue

According to Langenbeck (22) it is possible by the action of one molecule of isatin in the presence of oxygen to degrade several molecules of an amino acid, whereas in the absence of oxygen two molecules of isatin degrade only one molecule of the amino acid. Oxygen may be replaced by methylene blue. Thus, isatin (1 mole) in acetic acid solution in the presence of oxygen at 100°C. degraded alanine (7.7 moles) within 10 hr. The beneficial action of oxygen or methylene blue is due to the fact that, in consequence of secondary reactions, XIII is formed, which regenerates isatin by the action of oxygen or methylene blue.



XIII

4. Degradations effected in the presence of a base

Fluorenone, which was found to be inactive in a glycerol–water or dioxane–water mixture, is active in the presence of pyridine (27).

Baddar (4) found that when a mixture of *p*-nitrobenzaldehyde and alanine was refluxed with water, only traces of acetaldehyde were liberated; when the solvent was replaced by aqueous pyridine (75 per cent), the yield was "enormously" increased.

The effect on their degrading power of substituents in the benzene ring in isatins has been studied by Giovannini and Portmann (13), who worked in pyridine–water mixtures.

5. Degradations effected by aldehydes

Glyoxal and methylglyoxal (46) degrade α-amino acids rapidly; this is not astonishing, since they contain the group —$CO(C{=}C)_nCO$— (see page 263). Baddar (4, 5) and Moubacher (26) found that some aromatic aldehydes, e.g., nitrobenzaldehydes and piperonal, degrade α-amino acids in the presence of glycerol at about 100°C., but the velocity of this degradation is very small; therefore these monoaldehydes can hardly be described as active agents.

6. Biochemically important aldehydes and ketones as degrading agents

Hexoses: Glucose does not degrade α-amino acids when the reaction is carried out in an aqueous medium in the absence of oxygen (3) even at 100°C. The observed degradation in the presence of oxygen, especially when oxygen is passed through the system at 100°C., may be explained by assuming the oxidation of glucose to a substance containing the active —$CO(C{=}C)_nCO$— group. For example,

$$C_4H_9O_4CHOHCHO \xrightarrow[100°C.]{O_2} C_4H_9O_4COCHO$$

Akabori (2) claimed to have obtained a small amount of acetaldehyde by allowing glucose to react with alanine, in an aqueous medium, in the presence of glycerol, and in air free of carbon dioxide, for two months at room temperature. Schönberg and Moubacher (44) failed to find acetaldehyde when they worked according to Akabori's directions, apart from the fact that they worked in the absence of oxygen and light (12) and inhibited all microbiological action.

Akabori has also investigated the degrading power of hexoses in the absence of water. According to him glucose reacts with α-amino acids in the presence of glycerol at temperatures between 120°C. and 140°C.; during the experiment there distilled off aldehydes or ketones containing one carbon atom less than the amino acid used. This transformation could be carried out with $CH_3(CH_2)_4$-$CH(NHCH_3)COOH$, showing that an *unsubstituted* amino group is not necessary.

The interpretation of this reaction is made difficult, since under the conditions of the experiment sugars may not be thermostable (*cf.*, for example, the formation of glucosane from glucose (35)).

Synthetic antibiotics: The synthetic antibiotics 2-hydroxy-2′-methoxybenzil and *p*,*p*′-diaminobenzil (19) degrade α-amino acids under physiological conditions (46, 47). It seems possible that the antibiotic action of these substances is connected, *inter alia*, with their interference with the essential enzyme system of the bacterium *via* a Strecker degradation and/or that they destroy α-amino acids essential for the bacterium. The antibiotic action of *p*-benzoquinone derivatives, natural or synthetic, may be explained on this assumption.

Schönberg and Moubacher (42) have discussed the relationship between the degrading power of water-soluble substances and their bacteriostatic action as a working hypothesis in the search for new synthetic antibiotics and have in this connection discussed the antibiotic action of crystal violet.

Vitamin K_1 and 2-methyl-1,4-naphthoquinone: Vitamin K_1 degrades α-amino acids having a free amino group under physiological conditions (e.g., formation of benzaldehyde from α-aminophenylacetic acid). 2-Methyl-1,4-naphthoquinone, used in medicine in place of vitamin K_1, is also capable of bringing about such Strecker degradations (46, 48). As both substances contain the effective group —CO(C=C)$_n$CO—, this degrading power was to be expected. The decrease of the content of 2-methyl-1,4-naphthoquinone in present-day fodder preparations has been connected with the degrading action of this substance (18).

7. *Reaction mechanism of degradation by carbonyl compounds*

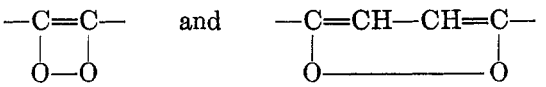
Wieland and Bergel (53) advanced the theory that α-amino acids are dehydrogenated by the action of carbonyl compounds to imino acids, which in the presence of water form aldehydes, carbon dioxide, and ammonia.

$$CH_3CH(NH_2)COOH \xrightarrow{[-2H]} CH_3C(=NH)COOH \xrightarrow{H_2O} CH_3CHO + NH_3 + CO_2$$

Dehydrogenation as an essential part of the reaction is also accepted by Langenbeck (21), who believes that the degradation of α-aminoisobutyric acid proceeds *via* a compound containing a monovalent nitrogen atom.

Wieland and Bergel's theory does not explain why substances of strong dehydrogenating power, such as methylene blue or azobenzene (46), do not degrade α-amino acids.

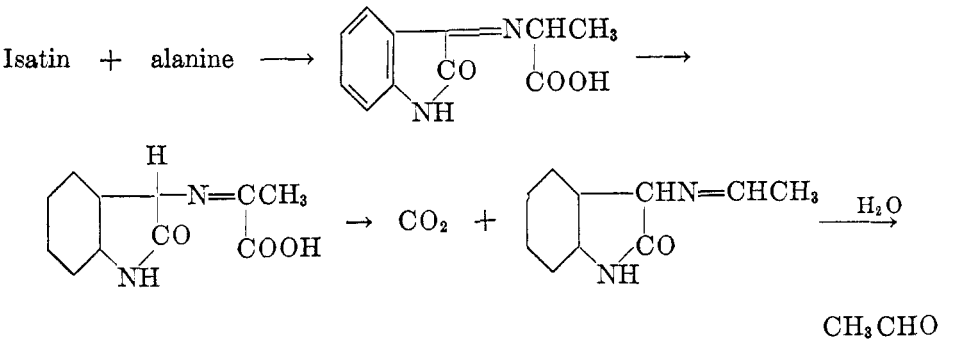
Akabori (2) pointed out the importance of the groups —COCO— and —COCH=CHCO— for the active reagents, and suggested that the degrading power of these groups is due to the formation of peroxides,



respectively, which dehydrogenate the α-amino acids.

A great advance in the theory of the Strecker degradation was made by Franke (11), who, taking alanine and isatin as examples, proposed reaction sequence A, thus suggesting that the degradation proceeds *via* a Schiff base.

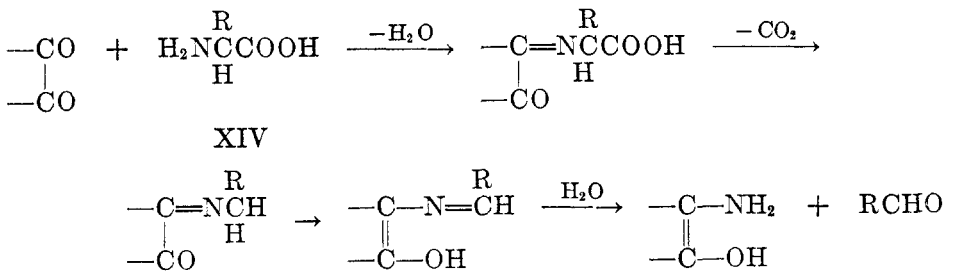
Reaction sequence A



This sequence (which necessitates a migration of a hydrogen atom from one carbon atom to another) does not explain why the monoketones which are listed in table 3 have no degrading power in a neutral aqueous medium.

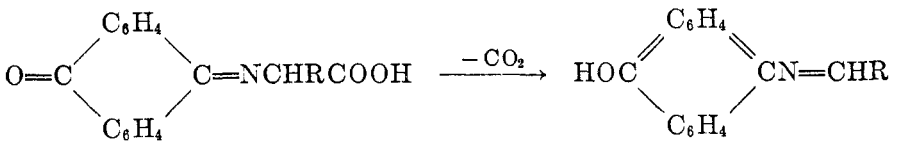
The importance of the grouping —CO(C=C)$_n$CO— as part of the degrading molecule is explained by reaction sequences B and C, recently advanced by Schönberg, Moubacher, and Mostafa (46); isatin and anthraquinone are taken as examples.

Reaction sequence B



In the case of anthraquinone, the essential part of the reaction involved in the degradation is as follows:

Reaction sequence C



A mechanism similar to those shown in reaction sequences B and C cannot be put forward for the action of α-amino acids on dibenzoylmethane, a fact which explains why this compound is incapable of bringing about the Strecker degradation.

It is shown from reaction sequences B and C that, in accordance with the

experimental results, the two hydrogen atoms of the amino group are essential for the degradation effected by ketones; e.g., sarcosine is not degraded by ninhydrin (46) and the same is true for proline, which is an *N*-substituted amino acid (14).

On the other hand, the hydrogen atom attached to the α-carbon atom may be substituted (*cf.* compound XIV); thus, aminoisobutyric acid yields acetone when treated with *p*-benzoquinone (21), methylglyoxal (34), ninhydrin, or *peri*-naphthindantrione (V) (46). The Strecker degradations of α-amino acids by ketones are complicated processes involving many steps—among others, formation of Schiff bases, elimination of carbon dioxide, hydrolysis, etc.—and it is doubtful whether there exists one and the same step which determines the rate of the reaction for all degradations. If the carbonyl group which is instrumental in the formation of the Schiff base is shielded by large groups, steric hindrance must be expected; in this case the formation of the Schiff base may be the step which determines the velocity of the degradation (*cf.* page 272).

8. Final fate of the amino group in Strecker degradations

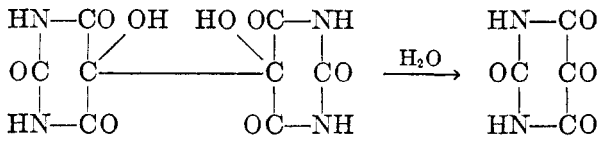
The fate of the amino group in Strecker degradations depends on the nature of the carbonyl compound employed as the degrading agent. (*a*) The amino group may be eliminated in the form of ammonia; this is the case when α-amino acids are degraded by the action of *peri*-naphthindantrione hydrate (XVII) (*cf.* reaction sequence E on page 271). (*b*) The amino group may become linked to the carbonyl compound which effects the degradation, converting it into an amino compound of similar structure; thus, alanine is formed when α-amino-phenylacetic acid is subjected to degradation by the action of pyruvic acid (15, 17).

Reaction sequence D

$$C_6H_5CH(NH_2)COOH + CH_3COCOOH \rightarrow C_6H_5CHO + CO_2 + CH_3CH(NH_2)COOH$$

9. Utilization of the degrading power of ketones in the elucidation of structure

Since so many facts have been collected in connection with the degrading power of ketones, it seems possible to use the results gained, especially the —CO(C=C)$_n$CO— (n = zero or an integer) "rule," as a tool in the elucidation of the constitution of carbonyl compounds. Alloxantin (XV) does not contain this "group"; nevertheless it is an active agent in the Strecker degradation (31). This is due to the fact that in warm solution it decomposes with the formation of alloxan (XVI), the latter being an active agent.



XV
Alloxantin

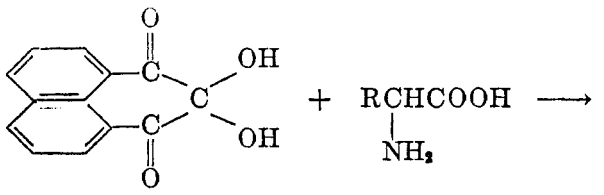
XVI
Alloxan

10. Quantitative methods based on Strecker degradations effected by polyketones

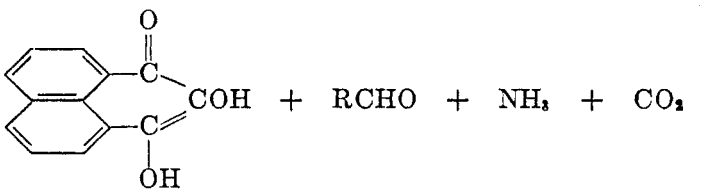
Van Slyke and coworkers (51) have described a highly accurate method for the determination of α-amino acids. A detailed report on this method, which consists in the determination of the amount of carbon dioxide evolved when ninhydrin and α-amino acids are heated in an aqueous medium, has been given by Sahyun (39). The method may also be used for microchemical work. Attention is also drawn to Virtanen's publication (52).

When ninhydrin is used in the determination of amino acids it cannot be regenerated. In view of the high cost of ninhydrin this is a disadvantage; therefore it has been proposed (25) to replace ninhydrin by *peri*-naphthindantrione hydrate (XVII). This substance, during the reaction, is transformed into XVIII, which separates out during the procedure; XVII can be obtained easily from XVIII by the action of bromine water.

Reaction sequence E



XVII



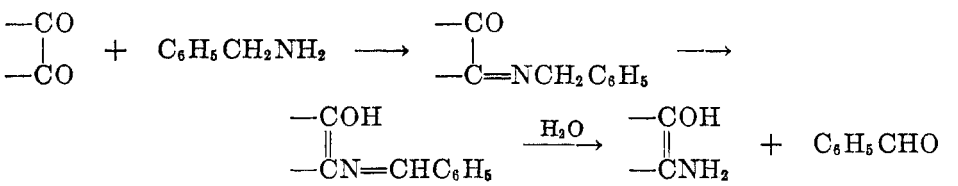
XVIII

The estimation of α-amino acids using XVII has been carried out successfully by measuring the amount of aldehydes, carbon dioxide, or ammonia evolved (25, 28, 32, 33).

B. REACTIONS ALLIED TO THE STRECKER DEGRADATION EFFECTED BY KETONES

1. Conversion of benzylamine to benzaldehyde

This change, which can be brought about by alloxan or isatin (50), proceeds according to the following scheme, which is closely related to reaction sequence B (see page 269).



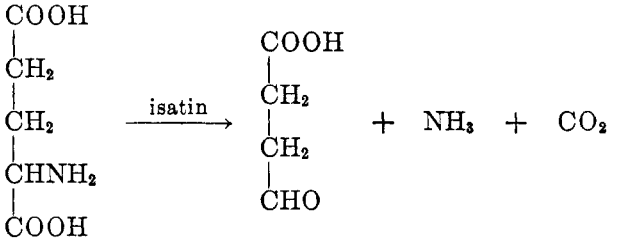
2,4,6-Trimethylbenzylamine and 2,6-dichlorobenzylamine do not form the corresponding benzaldehyde derivatives when treated with isatin under the same conditions under which benzylamine gives benzaldehyde; this was stated to be due to the fact that the formation of the Schiff base does not take place because of steric hindrance (43).

2. Transamination reactions

The intermolecular transfer of an amino group from an α-amino acid to an α-keto acid has become known as the "transamination reaction." The reaction scheme has already been given (*cf.* reaction sequence D on page 270) and the subject matter has been excellently reviewed by Herbst (15).

3. Action of methylglyoxal and peri-naphthindantrione on aspartic acid

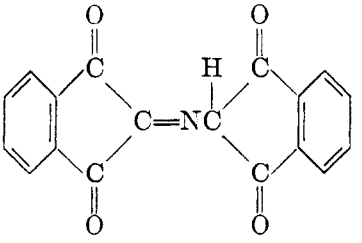
These reactions are related to the Strecker degradation; the difference is due to the formation of an aldehyde (acetaldehyde) containing two carbon atoms less than the amino acid. In this connection attention is drawn to the degradation of glutamic acid by isatin, which proceeds normally.



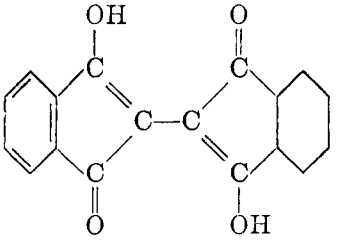
Glutamic acid

4. Nature of the color accompanying the degradation of amino acids by ninhydrin and peri-naphthindantrione hydrate

When α-amino acids are degraded by the action of ninhydrin (IIIa), there is produced a violet color which is believed to be due to the formation of XIX or its ammonium salts (14, 37, 38).



XIX



XX

Recently the matter has been reinvestigated and it has been found (30) that the color observed is due to a number of colored substances and not to one only. Some of these substances depend on the nature of the amino acid used, but the

formation of the violet bis-1,3-diketoindanyl (XX) was observed in all cases, e.g., when alanine and valine were degraded.

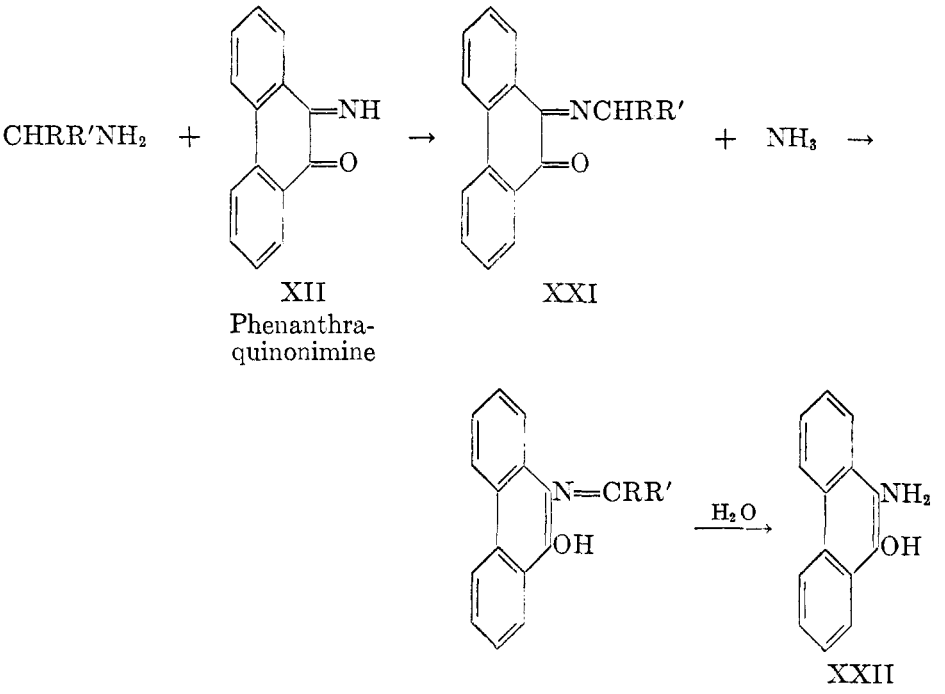
When degradations are carried out using *peri*-naphthindantrione hydrate (XVII), a red color is produced; among the colored products formed is dihydroxy-keto-*peri*-naphthindene (29) (XVIII) (see page 271).

5. The phenanthraquinonimine test for compounds containing the group $\rangle CHNH_2$

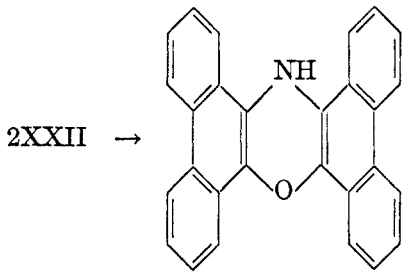
This characteristic and sensitive test is based on the formation of phenanthroxazine (XXIII) (tetrabenzophenoxazine) and is carried out by allowing the substance under investigation to react with phenanthraquinonimine (XII) in aqueous alcohol, in the presence of ammonium chloride. If the substance contains the group $\rangle CHNH_2$, then XXIII separates out; it is practically insoluble in low-boiling organic solvents and in water, but can be recrystallized from nitrobenzene. It forms characteristic crystals and gives with concentrated sulfuric acid a deep indigo-blue, nonfugitive color which can be detected in a concentration of 1 mg. in 300 ml. (thickness of layer = 1 cm.); the test can therefore be carried out as a micro-test.

The reaction sequences F and G are proposed for the formation of phenanthroxazine (R and R′ are alkyl or aryl groups or hydrogen).

Reaction sequence F



Reaction sequence G



XXIII
Phenanthroxazine

It is obvious from this scheme that the presence of the aliphatic hydrogen atom (as in XXI) is essential and that it is derived from the group $\rangle CHNH_2$. Substances not containing this group do not show the reaction.

There is a great difference between the test now described and that with "ninhydrin" (triketoindan hydrate (IIIa)). The latter reagent gives a violet color not only with substances containing the group $\rangle CHNH_2$, but also with ammonia, potassium cyanide, and an alcoholic solution of aniline even in the cold (36, 37).

C. DEGRADATIONS EFFECTED BY MISCELLANEOUS COMPOUNDS

Perbenzoic acid and benzoyl peroxide: In an aqueous medium at 100°C. these two substances (44) degrade α-amino acids with an unsubstituted amino group, e.g., isoleucine and α-aminoisobutyric acid in the case of benzoyl peroxide and leucine in the case of perbenzoic acid, but they fail with α-amino acids having a substituted amino group (e.g., sarcosine).

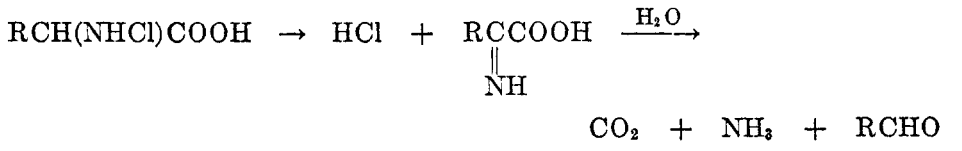
It is possible that benzoyl peroxide degrades after having been transformed into perbenzoic acid *via* hydrolysis. As it is known that per acids react with amino compounds with the formation of nitroso products (*cf.* the transformation of aniline to nitrosobenzene by the action of Caro's acid), the following mechanism is tentatively advanced; it explains why only amino acids having a free amino group are affected.

$$RCH(NH_2)COOH \xrightarrow{\text{per acid}} RCH(NO)COOH \rightarrow$$

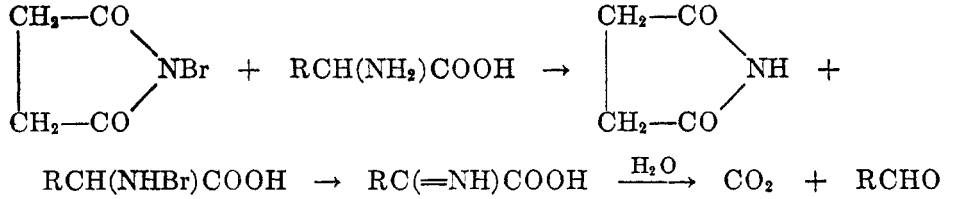
$$RC(=NOH)COOH \xrightarrow{H_2O} RCHO + CO_2$$

N-Chloroarylsulfonamides, N-bromosuccinimide, and allied substances: When *N*-chloroarylsulfonamides are allowed to react in an aqueous medium with α-amino acids having a free or a substituted amino group (e.g., aminophenylacetic acid or methylaminophenylacetic acid), a Strecker degradation occurs:

$$RCH(NH_2)COOH + ArSO_2NHCl \rightarrow RCH(NHCl)COOH + ArSO_2NH_2$$

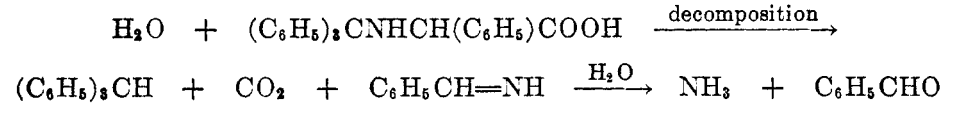


Recently it has been found (45) that a rapid Strecker degradation may be effected by allowing *N*-bromosuccinimide and *N*-bromophthalimide to react on α-amino acids in the presence of water; the reaction was carried out with alanine, valine, leucine, and phenylaminoacetic acid. The amino group may be substituted; e.g., sarcosine yields formaldehyde.

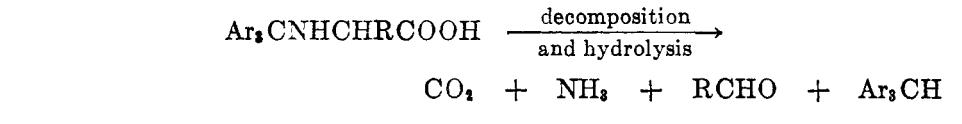


Triphenylmethane dyes and related substances: A number of triphenylmethane dyes, e.g., malachite green and crystal violet, are capable of degrading α-amino acids (42).

Triphenylcarbinol is also capable of degrading α-amino acids (e.g., phenylaminoacetic acid) in an acetic acid–water mixture.



The degrading power of triphenylcarbinol and of triphenylmethane dyes towards amino acids may be explained similarly.

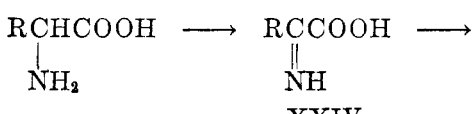


IV. Strecker Degradations Effected in the Presence of a Catalyst

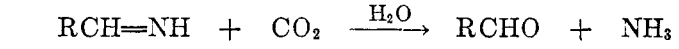
A. Degradations Effected in the Presence of a Catalyst and Oxygen

Wieland and Bergel (53) observed the degradation of α-amino acids having a free amino group in an aqueous medium and in the presence of oxygen and charcoal. They advanced reaction sequence H for this reaction. It is most probable that XXIV is an intermediate compound in these reactions, though it is improbable that the Strecker degradation effected by carbonyl compounds proceeds *via* XXIV (see page 269).

Reaction sequence H



XXIV



According to Bergel and Boltz (6, 7) *N*,*N*-dimethylglycine, *N*,*N*-dimethylleucine, and *N*,*N*-dimethylaminoisobutyric acid are degraded at room temperature by the action of oxygen, in the presence of animal charcoal, with the formation of dimethylamine, carbon dioxide, formaldehyde or acetone, respectively. *N*-Monomethylalanine yielded acetaldehyde more quickly than alanine itself. Bergel and Boltz discussed the possibility that the reaction proceeds *via* a peroxidic intermediate compound formed by the addition of oxygen to the nitrogen atom of the amino acids.

B. DEGRADATIONS EFFECTED IN THE ABSENCE OF OXYGEN

The velocity of the degradation at room temperature of α-amino acids by alloxan is greatly increased by the presence of palladium. The reactions were carried out in water in an atmosphere of nitrogen (53). Wieland and Bergel (53) have discussed the Strecker degradation in the presence of hydrogen acceptors (e.g., *m*-dinitrobenzene) in the absence of oxygen and have pointed out the biochemical significance of this reaction.

V. REFERENCES

(1) ABDERHALDEN, E.: Z. physiol. Chem. **252,** 81 (1938).
(2) AKABORI, S.: Ber. **66,** 143 (1933).
(3) AMBLER, J. A.: Ind. Eng. Chem. **21,** 47 (1929).
(4) BADDAR, F.: J. Chem. Soc. **1949** (supplement), S163.
(5) BADDAR, F.: J. Chem. Soc. **1950,** 136.
(6) BERGEL, F., AND BOLTZ, K.: Z. physiol. Chem. **220,** 20 (1933).
(7) BERGEL, F., AND BOLTZ, K.: Z. physiol. Chem. **215,** 25 (1933); **223,** 66 (1934).
(8) DAKIN, H. D.: J. Biol. Chem. **1,** 171 (1906).
(9) DAKIN, H. D., COHEN, J. B., DAUFRESNE, M., AND KENYON, J.: Proc. Roy. Soc. (London) **B89,** 232 (1916).
(10) FICHTER, F., AND KUHN, R.: Helv. Chim. Acta **7,** 167 (1924).
(11) FRANKE, W.: Biochem. Z. **258,** 280 (1933).
(12) GANASSINI, F.: Giorn. farm. chim. **61,** 439, 540 (1912).
(13) GIOVANNINI, E., AND PORTMANN, P.: Helv. Chim. Acta **31,** 1361 (1948).
(14) GRASSMANN, W., AND ARNIM, K.: Ann. **509,** 288 (1934).
(15) HERBST, R.: "The Transamination Reaction" in *Advances in Enzymology,* Vol. 4, p. 75. Interscience Publishers, Inc., New York (1946).
(16) HERBST, R., AND CLARKE, H.: J. Biol. Chem. **104,** 769 (1934).
(17) HERBST, R., AND ENGEL, B.: J. Biol. Chem. **107,** 505 (1934).
(18) KOETSVELD, E. E. VAN: Rec. trav. chim. **1950,** 1222.
(19) KUHN, R., BIRKOFER, L., AND MÖLLER, E.: Ber. **76,** 900 (1943).
KUHN, R., MÖLLER, E., AND WENDT, G.: Ber. **76,** 405 (1943).
(20) LANG, K.: Z. physiol. Chem. **241,** 68 (1936).

(21) LANGENBECK, W.: Ber. **61,** 942 (1928).
(22) LANGENBECK, W.: *Die organischen Katalysatoren und ihre Beziehungen zu den Fermenten,* 2nd edition, pp. 29–33. Springer Verlag, Berlin (1949).
(23) LANGHELD, K.: Ber. **42,** 392 (1909).
(24) MACFADYEN, D. A.: J. Biol. Chem. **150,** 251 (1943).
(25) MOUBACHER, R.: J. Biol. Chem. **175,** 187 (1948).
(26) MOUBACHER, R.: J. Chem. Soc. **1951,** 231.
(27) MOUBACHER, R.: J. Chem. Soc. **1951,** 1928.
(28) MOUBACHER, R., AND AWAD, W.: J. Biol. Chem. **179,** 915 (1949).
(29) MOUBACHER, R., AND AWAD, W.: J. Chem. Soc. **1949,** 1137.
(30) MOUBACHER, R., AND IBRAHIM, M.: J. Chem. Soc. **1949,** 702.
(31) MOUBACHER, R., AND OTHMAN, A.: J. Am. Chem. Soc. **72,** 2667 (1950).
(32) MOUBACHER, R., AND SINA, A.: J. Biol. Chem. **180,** 681 (1949).
(33) MOUBACHER, R., SINA, A., AWAD, W., AND OTHMAN, A.: J. Biol. Chem. **184,** 693 (1950).
(34) NEUBERG, C., AND KOBEL, M.: Biochem. Z. **188,** 197 (1927).
(35) PICTET, A., AND CASTEN, P.: Helv. Chim. Acta **3,** 645 (1920).
(36) RUHEMANN, S.: J. Chem. Soc. **97,** 1438 (1910).
(37) RUHEMANN, S.: J. Chem. Soc. **97,** 2025 (1910).
(38) RUHEMANN, S.: J. Chem. Soc. **99,** 792, 1486 (1911).
(39) SAHYUN, M.: *Outline of the Amino Acids and Proteins.* Reinhold Publishing Corporation, New York (1944).
(40) SCHÖNBERG, A., AND AWAD, W.: J. Chem. Soc. **1949,** 766.
(41) SCHÖNBERG, A., AND MOUBACHER, R.: J. Chem. Soc. **1949,** 212.
(42) SCHÖNBERG, A., AND MOUBACHER, R.: Science **109,** 547 (1949).
(43) SCHÖNBERG, A., AND MOUBACHER, R.: J. Chem. Soc. **1950,** 1422.
(44) SCHÖNBERG, A., AND MOUBACHER, R.: Unpublished data.
(45) SCHÖNBERG, A., MOUBACHER, R., AND BARAKAT, Z.: J. Chem. Soc., in press.
(46) SCHÖNBERG, A., MOUBACHER, R., AND MOSTAFA, A.: J. Chem. Soc. **1948,** 176.
(47) SCHÖNBERG, A., MOUBACHER, R., AND MOSTAFA, A.: Unpublished data.
(48) SCHÖNBERG, A., MOUBACHER, R., AND SAID, A.: Nature **164,** 140 (1949).
(49) STRECKER, A.: Ann. **123,** 363 (1862).
(50) TRAUBE, W.: Ber. **44,** 3145 (1911).
(51) VAN SLYKE, D. D., AND DILLON, R. T.: Proc. Soc. Exptl. Biol. Med. **34,** 362 (1936); Compt. rend. trav. lab. Carlsberg **22,** 480 (1938).
VAN SLYKE, D. D., MACFADYEN, D. A., AND HAMILTON, P.: J. Biol. Chem. **141,** 627, 671 (1941).
VAN SLYKE, D. D., MACFADYEN, D. A., AND HAMILTON, P.: J. Biol. Chem. **150,** 251 (1943).
MACFADYEN, D. A., HAMILTON, P., AND VAN SLYKE, D. D.: J. Biol. Chem. **145,** 387 (1942); **153,** 507 (1944); **150,** 231 (1943).
(52) VIRTANEN, A. I., LAINE, T., AND TOIVONEN, T.: Z. physiol. Chem. **266,** 193 (1940).
(53) WIELAND, H., AND BERGEL, F.: Ann. **439,** 196 (1924).