(I) have been tried without success. Dicyclohexenyl (4.5 cc.)[6] and 1,2-naphthoquinone (10.4 g.) condensed at 180° to form an unworkable black resin, and 3-bromo-1,2-naphthoquinone (1.6 g.) did not react at all with this hydrocarbon (1.1 g.) when heated at 100° for four hours in the presence of *sym*-tetrachloroethane[7] (10 cc.). The potassium derivative of ethyl cyclohexanone-*o*-carboxylate could not be coupled with β-(9-phenanthryl)-ethyl chloride, even on prolonged heating,[8] and finally the fact may be recalled,[9] that 9-cyclohexenylphenanthrene does not react with maleic anhydride to form a derivative of 1,2,3,4-dibenzophenanthrene.

Summary

By interaction between 2-methylcyclohexanone and the Grignard derivative of β-(9-phenanthrylethyl) chloride and subsequent cyclization, a spirane is formed instead of the expected octahydro-methyl-1,2,3,4-dibenzophenanthrene. Its dehydrogenation gave small amounts of an aromatic hydrocarbon. Several other methods of synthesis also failed.

REHOVOTH, PALESTINE RECEIVED MARCH 4, 1938

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[6] Compare Weizmann, Bergmann and Berlin, THIS JOURNAL, **60**, 1331 (1938).

[7] Compare, for this method, Fieser and Dunn, *ibid*,, **59**, 1016, 1021, 1024 (1937).

[8] With this reaction, we intended to utilize the method of Ruzicka, Ehmann, Goldberg and Hoesli [*Helv. Chim. Acta*, **16**, 833 (1933)] for the synthesis of chrysene and 1,2-cyclopentenophenanthrene.

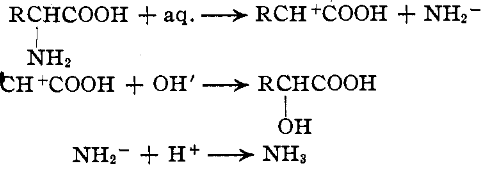
[9] E. Bergmann and F. Bergmann, THIS JOURNAL, **59**, 1443 (1937).

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

The Photochemical Deamination of Amino Acids in Water Solution. II

BY CH. WEIZMANN, Y. HIRSHBERG AND ERNST BERGMANN

In the first paper on the subject,[1] we were able to demonstrate that under the influence of ultraviolet light water solutions of amino acids undergo hydrolysis according to the scheme



$$\mathrm{R}\underset{\mathrm{NH_2}}{\underset{|}{\mathrm{C}}}\mathrm{HCOOH} + \mathrm{aq.} \longrightarrow \mathrm{RCH^+COOH} + \mathrm{NH_2^-} \qquad \text{(a)}$$

$$\mathrm{RCH^+COOH} + \mathrm{OH'} \longrightarrow \mathrm{R}\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\mathrm{HCOOH} \qquad \text{(b)}$$

$$\mathrm{NH_2^-} + \mathrm{H^+} \longrightarrow \mathrm{NH_3} \qquad \text{(c)}$$

In order to see how the nature of the group R influences the speed of the reaction, we compared alanine and phenylalanine under identical conditions. Phenylalanine decomposes about 2.7 times as quickly as alanine, in 0.1 *N* solution, and 2.2 times as quickly in 0.05 *N* solution. This influence of the phenyl group may be due to two effects, to its loosening the C–N bond and to the increase in light absorption,[2] both effects perhaps being connected in some way. The necessary measurements could be made only in the first stage of the reaction, as phenylalanine undergoes a side reaction, leading to an insoluble coating on the quartz walls and to the formation of an unpleasantly smelling volatile product. In the first minutes of irradiation, however, only ammonia is formed, according to the above scheme. The same complication as with phenylalanine occurs in the case of phenylglycine, $C_6H_5CH(NH_2)COOH$, the decomposition of which therefore could not be studied. Apparently, these side reactions are due to the presence of the aromatic nucleus, as similar observations have been made before with tyrosine solutions.[3]

The constitutional change brought about by coupling alanine with glycine to form alanylglycine also increases the speed of the photochemical deamination. Alanylglycine is hydrolyzed 4.2 times as quickly as alanine in 0.1 *N* solution, and 2.6 times as quickly in 0.05 solution. It is difficult to explain this difference, but it may be assigned to the greater distance between the amino and the free carboxyl group enhancing the ionization of the C–N bond, or to the increased light absorption[4] or to both effects. It may be added that we think it safe to ascribe the ammonia formed exclusively to the decomposition of the $-C-NH_2$ and not of the amide group, since the amide group, as far as we know, is much stabler toward photochemical hydrolysis.[5] It appears that peptides are attacked in the same way as amino

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[1] Weizmann, Bergmann and Hirshberg, THIS JOURNAL, **58**, 1675 (1936).

[2] Compare Allen, Steiger, Magill and Franklin, *Biochem. J.*, **31**, 195 (1937).

[3] Compare Part I. The ultraviolet absorption spectra of tyrosine and phenylalanine are practically identical: Feraud, Dunn and Kaplan, *J. Biol. Chem.*, **112**, 323 (1935).

[4] Magill, Steiger and Allen, *Biochem. J.*, **31**, 188 (1937).

[5] Compare, *e. g.*, the experiments of Paternò, *Gazz. chim. ital.*, **44**, I, 237 (1914). Allen, Steiger, Magill and Franklin[2] have stated recently that in acylated amino acids and peptides hydrolysis of the –CO–NH-group occurs on irradiation. While that may be true in the case of acylated amino acids, which do not contain the amino group necessary for photolysis, there apparently is no need for that assumption with regard to peptides.

acids, although Guillaume and Tanret[6] have failed previously to detect photolysis of peptides.

The quantum yield of the reactions has been studied with greater accuracy. The measurements were carried out with a vertical mercury arc lamp, which had four jackets.[7] The first and the fourth served for cooling with running water, in the second and third we had (a) water and monochloroacetic acid, or (b) the amino acid and monochloroacetic acid of equal normalities. The difference in the decomposition of monochloroacetic acid gave us the light absorbed in the amino acid layer, and its comparison with the degree of decomposition as determined by the amount of liberated ammonia gave the desired quantum yield. (In view of our preparative experiments,[1] it seemed safe to assume that the liberation of ammonia (or trimethylamine) is the only reaction occurring). Naturally, the jacket walls have to be kept extremely clean, as otherwise the translucence would not be identical in all experiments. Our experiments showed that in the case of alanine and glycine the quantum yield is equal to 0.09 and 0.1, respectively, while for betaine 0.06 has been observed. The ratio between the amino acids and betaine is about the same as found in Part I, and may be explained as suggested there,[8] although the absolute values according to our new more accurate measurements are definitely lower. The low absolute values are due, at least partly, to the increase in absorption, which sets in during irradiation according to Allen, Steiger, Magill and Franklin.[9]

The hydrolysis reaction we observe in the cases studied may be interesting from a biochemical point of view, as its occurrence in green plants may account for the relatively wide distribution in them of α-hydroxy acids. Other ways for the hydrolytic fission of amino acids, in any case, seem not to be available to the cell, as has been pointed out already in Part I. It has been suggested occasionally that bacteria are able to produce hydrolysis of the above type,[10] but observations like that of Otani and Ichihari,[11] that *Oospora lactis* produces (+)-lactic acid from both the forms of alanine, suggest that the amino acid is first oxidatively de-aminated and the keto acid formed subsequently hydrogenated. The same holds true for higher animals. Kotake, Kotake and Taniguchi,[12] *e. g.*, obtained after tyrosine feeding *p*-hydroxyphenyllactic acid along with *p*-hydroxyphenylpyruvic acid. For the classical photolytic conversion of amino acids into aldehydes in the presence of oxygen, on the other hand, it seems justified to assume hydroxy acids as intermediary products, although no definitive proof can be advanced.[13] The reducing properties of irradiated amino acid solutions,[14] *e. g.*, could be attributed to hydroxy acid formation.

Experimental

COMPARATIVE PHOTOLYSIS OF PHENYLALANINE AND ALANINE

Time, min.	Cc. of 0.1 N NH_3 formed from alanine	Cc. of 0.1 N NH_3 formed from phenylalanine
	(a) 0.1 N solution (50 cc.)	
5	0.16	0.55
10	.31	.90
15	.45	1.25
20	.59	1.50
25	.72	1.70
30	.88	1.91
	(b) 0.05 N solution (50 cc.)	
5	0.18	0.41
10	.25	.72
15	.38	.90
20	.50	1.08
25	.62	1.29
30	.74	1.47

COMPARATIVE PHOTOLYSIS OF ALANYLGLYCINE AND ALANINE

Time, hours	Cc. of 0.1 N NH_3, formed from alanine	Cc. of 0.1 N NH_3 formed from alanylglycine
	(a) 0.1 N solution (25 cc.)	
1	1.91	8.65
2	3.54	16.80
3	4.99	21.13
4	6.25	25.46
5	8.23	29.24
	(b) 0.05 N solution (25 cc.)	
1	1.55	3.95
2	2.91	6.50
3	4.28	9.55
4	5.52	14.26
5	6.55	17.58

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(6) Guillaume and Tanret, *Compt. rend. acad. sci.*, **201**, 1057 (1935); compare *Bull. soc. biol.*, **18**, 571 (1936).

(7) For a similar device see Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **18B**, 124 (1932).

(8) Compare the analogous views expressed for the case of acrolein by Thompson and Linnett, *J. Chem. Soc.*, 1452 (1935).

(9) Thanks are due to the Referee for drawing our attention to that point.

(10) See, *e. g.*, Ehrlich and Jacobsen, *Ber.*, **44**, 888 (1911).

(11) Otani and Ichihari, *Folia Jap. Pharmacol.*, **1**, 397 (1925); quoted by Heigeuer, *Centralbl. Bakt.*, *II*, **93**, 83 (1935).

(12) Kotake, Kotake and Taniguchi, *J. Biochem.*, **18**, 395 (1933). Compare Sasaki and Otsuka, *J. Biol. Chem.*, **32**, 533 (1917); Kotake, Chikano and Ichihara, *Z. physiol. Chem.*, **143**, 218 (1925).

(13) Compare Ganassini, *Giorn. Farm. Chem.*, **61**, 439, 481 (1912); *Chem. Centralbl.*, **84**, I, 153 (1913).

(14) Wels, *Naunyn-Schmiedeberg's Archiv*, **181**, 147 (1936).

Quantum Yield of the Glycine Photolysis.—The inner chamber of the quartz lamp contained 115 cc. of water or of the 1 N amino acid solution, respectively, the outer one 200 cc. of 1 N monochloroacetic acid solution. Owing to the fact that glycolic acid as formed from monochloroacetic acid is unstable by itself, the amino acid solution was irradiated for one hour, while during only half of this time the outer jacket was filled with the chloro acid solution. 200 cc. of the 1 N monochloroacetic acid, *e. g.*, gave within thirty minutes 150 cc. of 0.1 N Cl^-, when irradiated through water, and 110 cc. of 0.1 N Cl^-, when irradiated through glycine solution. During one hour of irradiation, this glycine solution liberated 8.8 cc. of 0.1 N ammonia; quantum yield $8.8/2(150 - 110) = 0.11$. The following figures have been obtained in a number of analogous experiments: 0.11, 0.10, 0.09, 0.10, 0.09, 0.10, 0.12, 0.12, 0.11; average, 0.10.

Quantum Yield of the Alanine Photolysis.—The following figures have been determined: 0.088, 0.086, 0.094, 0.085, 0.087, 0.084; hence average, 0.087.

Quantum Yield of the Betaine Photolysis.—The following data have been secured: 0.065, 0.066, 0.064, 0.064, 0.062; hence average, 0.064.

Summary

The photolysis of alanine in water solution has been compared with that of phenylalanine and alanylglycine; in both cases the speed of the reaction is increased with regard to the velocity of the alanine decomposition. In the case of phenylalanine (and of phenylglycine), secondary reactions also take place, obviously due to the presence of the phenyl group.

The biological importance and the unique position of this photolysis is stressed, no other biological ways of amino acid hydrolysis being known.

The quantum yield of the photolytic fission has been more accurately redetermined in the cases of glycine, alanine and betaine; again, a markedly lower value has been obtained for betaine.

REHOVOTH, PALESTINE RECEIVED MARCH 12, 1938

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

Dipole Moments and Molecular Structure. XIX.[1] Dipole Moments of Anthracene Derivatives and the Stereochemical Mechanism of Addition and Splitting Reactions in the Anthracene Series

BY ERNST BERGMANN AND ANNA WEIZMANN

Recently,[2] one of the present authors, has given a classification of halogen additions to double bonds. Since all mechanisms concerned involve a two-step reaction, it is understood that usually the entering halogen atoms (or ions) arrange themselves as remotely as possible from each other ("*trans*-addition").[2a] Therefore, we think it worth while communicating that the addition of chlorine[3] to 1,5-dichloroanthracene (to form I) and 9,10-diphenylanthracene (to form II) is a pure *cis* reaction,[4] the dichlorides formed having dipole moments of 3.7 and 3.0, respectively. We are inclined to assume that this unexpected course is due to steric factors. The anthracene model shows that a chain of two atoms easily may form a bridge between the 9,10-positions of the anthracene nucleus, so that the *chlorine molecule* will be able to enter the anthracene molecule as such. From this point of view, the chlorination parallels the "Einlagerung" of oxygen molecules (III)[5] or of substances of the maleic anhydride type (IV).[6]

A similar explanation for the course of an ad-

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[1] Part XVIII: Bergmann and Weizmann, *Trans. Faraday Soc.*, **32**, 1327 (1936).

[2] E. Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937); *cf.* Roberts and Kimball, THIS JOURNAL, **59**, 947 (1937).

[2a] For a review see G. Wittig, "Stereochemie," Akad. Verlagsgesellschaft, Leipzig, 1930, pp. 120 ff.

[3] The slight solubility of the corresponding dibromide prevented us from assigning a configurational formula; 0.2431 g. in 20 cc. of α-methylnaphthalene at 52.10° showed no visible difference in the dielectric constant from the pure solvent.

[4] The same structure has been assigned to (I) by de Barry Barnett.[12]

[5] Compare also for references, Dufraisse and Le Bras, *Bull. soc. chim.* [5] **4**, 349 (1937); Willemart, *ibid.*, **357**, 510 (1937).

[6] Diels and Alder, *Ann.*, **486**, 191 (1931); *Ber.*, **64**, 2116 (1931); Clar, *ibid.*, **64**, 1676, 2194 (1931); Cook, *J. Chem. Soc.*, 3273 (1931). Compare Bergmann and Fujise, *Ann.*, **480**, 188 (1930).