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).

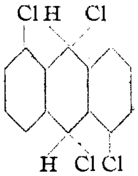
[2a] For a review see G. Wittig, "Stereochemie," Akad. Verlagsgesellschaft, Leipzig, 1930, pp. 120 ff.

[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.

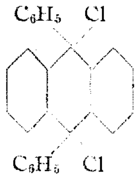
[4] The same structure has been assigned to (I) by de Barry Barnett.[12]

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

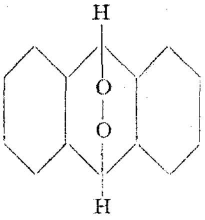
[6] Diels and Alder, *Ann.*, **486**, 191 (1931); *Ber.*, **64**, 2116 (1931); Clar, *ibid.*, **64**, 1676, 2194 (1931); Cook, *J. Chem. Soc.*, 3273 (1931). Compare Bergmann and Fujise, *Ann.*, **480**, 188 (1930).



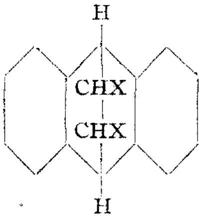
I



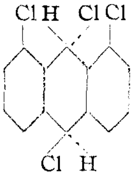
II



III



IV



V

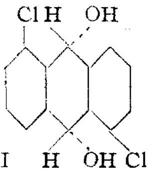
dition reaction has been given recently by K. Ziegler and co-workers[7] in the case of the lithium addition to butadiene, *cis* reaction taking place because of the oriented adsorption of the hydrocarbon on the metal surface.

1,8-Dichloroanthracene apparently adds chlorine "normally" in *trans* reaction, the 1,8-dichloroanthracene-9,10-dichloride (V) having an even smaller dipole moment (2.4*D*) than the parent substance ($\mu = 3.2D$), while the *cis* isomeride of (V) should have a markedly higher moment (4.5–5*D*).[8] Perhaps the close proximity of the two halogen atoms in the positions 1 and 8 prevents the above mechanism from being valid in this case.[9]

With regard to the numerical values observed, two remarks may be made. It is not clear why I and II do not have identical moments, the moments of di- and triphenylchloromethane being nearly equal:[10] one would suggest an inductive influence of the nuclear halogen atoms in (I)[11] (see below). The unexpectedly high difference in moments between 1,8-dichloroanthracene and its 9,10-dichloride may be due to the presence in the former substance of an ortho-chlorinated styrene system, the effect of which has been studied before by the authors.[1]

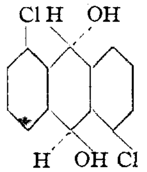
In studying the splitting reactions of dihalides of types (I) and (V), de Barry Barnett and his co-workers[12] have assumed that only *cis* reactions are likely to occur, divergent observations being explained by previous steric rearrangement of the dihalide or by its stereochemical inhomogeneity. These suggestions seem unsatisfactory. First of all, the substances used in our work were well-crystallized and certainly homogeneous. Second, it is difficult to understand that heating of 1,8-dichloroanthracene dichloride, *e. g.*, by itself or in presence of boiling xylene or cymene gives different results (removal of hydrogen chloride or chlorine, respectively), if these differences are due to previous rearrangement in one case. Third in terms of Barnett's hypothesis, it is unexplainable why under the above conditions 1,5,9-trichloroanthracene-9,10-dichloride loses hydrogen chloride while 1,8,10-trichloroanthracene-9,10-dichloride loses chlorine under the influence of potassium hydroxide. We prefer the view that there is *no visible rule governing the steric course of the splitting reaction.*

Obviously, in substitution reactions, configurational inversion may occur. One example is that 9,10-diphenyl-9,10-dihydroxy-9,10-dihydroanthracene, a homogeneous substance, reacts with dimethylaniline to yield two isomeric forms of 9,10-diphenyl-9,10-di-(*p*-dimethylamidophenyl)-9,10-dihydroanthracene.[13] 1,5-Dichloroanthracene 9,10-dibromide, on interaction with water in presence of acetone and calcium carbonate, affords according to E. de Barry Barnett[12] two isomeric 1,5-dichloro-9,10-dihydroxy-9,10-dihydroanthracenes (m. p. 210 and 244°, respectively)



VI

and



VII

We have measured the moment of the lower-melting form and found 2.95*D*; for the isomeric form, due to its low solubility, we can only say that its moment is smaller. Therefore, the sub-

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(7) Ziegler, Haeffner and Grimm, *Ann.*, **528**, 101 (1937).

(8) Moment of 1,8-dichloroanthracene, plus moment of (I) or (II) perpendicular to it. Compare the dipole moment of *trans*-1,4-dihalogenocyclohexanes: Halmoey and Hassel, *Z. physik. Chem.*, **B15**, 472 (1932).

(9) The instability of the 9,10-dihalides of anthracene itself made the determination of their dipole moments impossible.

(10) Weissberger and Saengewald, *Z. physik. Chem.*, **B20**, 145 (1935); Bergmann, Engel and Wolf, *ibid.*, **B17**, 81 (1932).

(11) Weissberger and Hampson, *Trans. Faraday Soc.*, **30**, 884 (1934); *J. Chem. Soc.*, 393 (1936); THIS JOURNAL, **58**, 2111 (1936).

(12) E. de Barry Barnett, *Rec. trav. chim.*, **43**, 530 (1924); **44**, 217, 728, 818, 894 (1925); **45**, 68, 558 (1926).

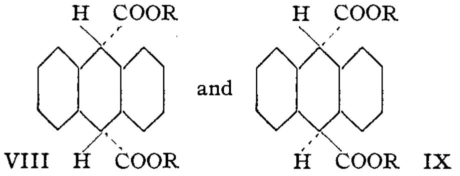
(13) Haller and Guyot, *Compt. rend.*, **140**, 343 (1905).

TABLE I

τ	ρ	ϵ	n^2	$P_{1/2}$	$P_{E_{1/2}}$	P	P_E	P_{A+O}
1,5-Dichloroanthracene-9,10-dichloride (I), *t* 24.8°, α-methylnaphthalene								
0	1.0155	2.6818	2.6044	50.2322	48.7233	....	...	→
0.00883	1.0208	2.8082	2.6053	52.8851	49.0189	350.84	82.21	268.63
0.01166	1.0224	2.8774	2.6063	54.2325	49.1322	393.44	83.80	309.64
$P^{\infty}_{A+O} = 289.1$ (average) $\mu = 3.7D$								
1,8-Dichloroanthracene-9,10-dichloride (V), *t* 45.0°, dioxane								
0	1.0239	2.2250	1.9901	24.9189	21.3265	....	...	→
0.00731	1.0325	2.2914	1.9997	26.1382	21.7105	191.69	73.86	117.84
0.00841	1.0338	2.2963	2.0009	26.2488	21.7630	183.12	73.22	109.90
$P^{\infty}_{A+O} = 119.0$ $\mu = 2.4D$								
1,8-Dichloroanthracene, *t* 23.4°, dioxane								
0	1.0316	2.2347	2.0138	24.8724	21.5456	....	...	→
0.00557	1.0362	2.3270	2.0249	26.3069	21.8430	286.05	74.96	211.09
$\mu = 3.2D$								
9,10-Diphenylanthracene-9,10-dichloride (II), *t* 38.2°, benzene								
0	0.8569	2.2374	2.2337	26.5794	26.5265	....	...	→
0.00228	.8636	2.2685	2.2391	27.0950	26.6506	252.41	80.84	171.53
0.00437	.8698	2.2583	2.2240	27.6081	26.4575	214.455	74.09	140.36
$P^{\infty}_{A+O} = 175$ $\mu = 3.0D$								
1,5-Dichloro-9,10-dihydroxy-9,10-dihydroanthracene, m. p. 210° (VI), *t* 25.4°, dioxane								
0	1.0296	2.2364	2.0141	24.9441	21.5925	....	...	→
0.00245	1.0322	2.2692	2.0171	25.4824	21.7010	244.24	65.70	178.45
0.00272	1.0335	2.2697	2.0178	25.4718	21.6985	218.67	60.50	158.17
0.00547	1.0354	2.2994	2.0226	25.9944	21.8650	217.09	71.44	145.65
$P^{\infty}_{A+O} = 180.0$ $\mu = 2.95D$								
Dimethyl *cis*-9,10-dihydroanthracene-9,10-dicarboxylate (VIII), *t* 23.6°, benzene								
0	0.8744	2.2767	2.2396	26.6296	26.0812	....	...	→
0.00811	.8829	2.3597	2.2497	28.1767	26.5681	217.40	86.12	131.28
0.01669	.8919	2.4737	2.2557	30.1513	27.0081	237.62	81.61	156.01
$P^{\infty}_{A+O} = 143.65$ (average) $\mu = 2.6D$								
Dimethyl *trans*-9,10-dihydroanthracene-9,10-dicarboxylate (IX), *t* 24.2°, benzene								
0	0.8737	2.2755	2.2396	26.6331	26.0965	....	...	→
0.00802	.8818	2.3078	2.2427	27.4575	26.4918	127.03	75.36	51.67
0.01143	.8852	2.3385	2.2485	28.0544	26.7218	150.93	80.79	70.14
$P^{\infty}_{A+O} = 60.90$ (average) $\mu = 1.7D$								
1-Chloroanthraquinone, *t* 29.60°, dioxane								
0	1.0272	2.2312	2.0042	24.9284	21.4852	....	...	→
0.01397	1.0382	2.3180	....	26.5094	.....	138.03	...	68.75
0.01707	1.0413	2.3567	2.0338	27.1495	21.3440	148.48	69.28	79.20
$P^{\infty}_{A+O} = 74.0$ (average) $\mu = 1.9D$								

stance of m. p. 210° would be the *cis* diol, the other one the *trans* form, in accordance with Barnett's assumptions. The formation of the *cis* diol from the *trans* dibromide involves a single inversion, the formation of the *trans* form none, or a double one.

In connection with these experiments, the two isomeric dimethyl 9,10-dihydroanthracene-9,10-dicarboxylates described by Schlenk and Bergmann[14] have been investigated. Their dipole moments have been found to be 2.6*D* for the β-ester and 1.7*D* for the α-ester, respectively. As in the case of diethyl maleate and fumarate,[15] the lower moment should correspond to the *trans* isomeride.



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[14] Schlenk and Bergmann, *Ann.*, **463**, 134 ff. (1928).

[15] Smyth and Walls, THIS JOURNAL, **53**, 527 (1931). Compare Briner and co-workers, *Helv. Chim. Acta*, **19**, 1354 (1936).

This is in accordance with the fact that alkali converts the β- into α-acid, probably *via* an enol form.

Finally, the dipole moment of 1-chloroanthraquinone (1.9*D*) may be recorded, the rather high value probably being due to induction or resonance effects.

Experimental

1. Materials

1,5-Dichloroanthracene.[16]—Commercial 1,5-dichloroanthraquinone (50 g.) is heated with 20% ammonia solution (1 liter) on a steam-bath, and zinc dust (250 g.) gradually added. The mass, first blood-red, becomes slightly reddish, it is filtered after standing for ten hours and extracted several times, while still wet, with acetone. The acetone residue on crystallization from butanol gives yellow 1,5-dichloroanthracene, m. p. 187°, while a colorless product remains in the mother liquors; from petroleum ether this gives needles, m. p. 102–103°. It is 1,5-dichloro-9-hydroxy-9,10-dihydroanthracene (Calcd. for $C_{14}H_{10}OCl_2$: C, 63.4; H, 3.8. Found: C, 63.0, 63.3; H, 4.0, 4.0). On dissolving this in hot propyl alcohol and adding a few drops of concd. hydrochloric acid, 1,5-dichloroanthracene precipitates in a pure state. The most convenient method, therefore, is to dissolve the crude acetone residue in the minimum amount of propyl or butyl alcohol and to add a few drops of hydrochloric acid; yield 30 g.

1,5-Dichloroanthracene-9,10-dichloride (I) was prepared according to Liebermann and Beudet[17] at 0° from 1,5-dichloroanthracene and an excess of chlorine solution in carbon tetrachloride. After three hours the product was collected, washed with ligroin and dried; m. p. 214–215° (Calcd. for $C_{14}H_8Cl_4$: C, 52.8; H, 2.5. Found: C, 52.3; H, 2.7). The bromide was prepared in the same way; m. p. 220° (after short sintering).

1,8-Dichloroanthracene from toluene, m. p. 185°, and its **dichloride** (V), m. p. 184° (dec.), were obtained in the same way as the 1,5-compounds, **9,10-diphenylanthracene-9,10-dichloride** (II) from 9,10-diphenylanthracene and chlorine or more conveniently according to Bergmann and Blum-Bergmann.[18] 1-Chloroanthraquinone (commercial sample) was recrystallized.

1,5-Dichloro-9,10-dihydroxy-9,10-dihydroanthracenes.[12] (a) *cis* **Isomeride.**—1,5-Dichloroanthracene-9,10-dibromide (16 g.) was heated with acetone (190 cc.) and water (120 cc.) for four hours. The filtered solution (residue mainly 1,5-dichloroanthracene) deposits a yellowish precipitate which is carefully recrystallized from toluene to a constant m. p. of 210–212°; colorless prisms; yield 1.65 g. (b) *trans* **Isomeride.**—1,5-Dichloroanthracene-9,10-dibromide (31 g.), acetone (300 cc.) and calcium carbonate (8.5 g.) were boiled for eight hours. The insoluble product (the solution contains mainly the *cis* diol) was collected and recrystallized several times from xylene; fractionation removed a small quantity of a yellow substance (apparently 1,5-dichloroanthracene); m. p. 241°; yield 0.5 g.

The *trans* compound was too slightly soluble for a series of measurements. At a molar fraction of 0.0272, the dioxane solutions of the two isomerides had the same refractive index, but with the *trans* compound the dielectric properties of the solution were not markedly different from those of the pure solvent.

2. Measurements

The significance of the figures is as in previous communications. The data for α-methylnaphthalene have been reported by Bergmann and Schuetz.[19]

Summary

Dipole moment measurements reveal that the addition of chlorine to 1,5-dichloroanthracene and 9,10-diphenylanthracene is a *cis* reaction; it is suggested that, in contradistinction to the usual behavior, the chlorine *molecule* is added. 1,8-Dichloroanthracene adds chlorine in *trans* reaction. The splitting reactions of anthracene-9,10-dihalides show no recognizable regularity.

Hydrolysis of 1,5-dichloroanthracene-9,10-dibromide is accompanied, at least partially, by Walden inversion; the dipole moment of the corresponding *cis* diol has been measured. On the basis of the dipole moments, the spatial arrangement of the isomeric dimethyl 9,10-dihydroanthracene-9,10-dicarboxylates has been determined.

REHOVOTH, PALESTINE RECEIVED APRIL 30, 1938

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[16] *Cf.* v. Braun and Bayer, *Ber.*, **59**, 914 (1928).

[17] Liebermann and Beudet, *ibid.*, **47**, 1011 (1914).

[18] Bergmann and Blum-Bergmann, THIS JOURNAL, **59**, 1439 (1937).

[19] Bergmann and Schuetz, *Z. physik. Chem.*, **B19**, 398 (1932).