with 5,6-benzo-2,3-dihydrobenzonaphthene (m. p. 76–77°) the melting point was 72–75°.

Attempt to Synthesize 9,10-Cyclopentenophenanthrene.—To the ice-cold Grignard reagent prepared from 11.3 g. of *o*-bromobiphenyl in 30 cc. of ether was added 4.1 g. of cyclopentanone, drop by drop. The mixture was kept at 0° for three hours and then hydrolyzed with ice-cold ammonium chloride solution. The residue obtained by evaporation of the ether crystallized when rubbed with petroleum ether. The crystals (2.6 g.) were filtered off, digested with 25 cc. of cold methanol and the solution of the carbinol was filtered from a small amount (0.2 g.) of insoluble material. The methanol was evaporated and the residue was recrystallized from benzene–petroleum ether, whereby 1.05 g. of **1-(*o*-biphenyl)-1-cyclopentanol (XIV)** was obtained as large, colorless, diamond-shaped tablets; m. p. 90.5–91.5°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.6; H, 7.7.

The petroleum ether solution of the original mixture deposited 1.4 g. of unidentified material as colorless leaflets melting at 157°.

An intimate mixture of the aforementioned carbinol (0.92 g.) and powdered potassium acid sulfate (1.5 g.) was heated for one hour at 160°. The mixture was digested with water and benzene, the benzene solution was separated, evaporated to dryness and the residue was distilled at 140–145° at 0.5 mm. The **1-(*o*-biphenyl)-Δ^1-cyclopentene (XV)** (0.8 g.), which was obtained as a colorless, mobile liquid, was dissolved in 10 cc. of ice-cold carbon disulfide and treated with 1.2 g. of powdered aluminum chloride. After five hours at 0°, the colorless, supernatant liquid was decanted from the sludge, washed with dilute hydrochloric acid and evaporated. The **9-fluorylspirocyclopentane (XVI)** crystallized from alcohol as colorless needles; weight, 0.42 g.; m. p. 91°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.5; H, 7.3.

Heating with sulfur at 250° for six hours, or with an equal weight of platinum black at 300° in an atmosphere of carbon dioxide for seven hours, gave back the hydrocarbon unchanged except for a small amount of decomposition products. After treatment with twice its weight of selenium in a sealed tube at 240° for fifteen hours and then at 310–320° for three hours, 90% of the hydrocarbon was recovered unchanged.

Summary

β-(1-Phenanthryl)-propionic acid, β-(2-phenanthryl)-propionic acid, β-(3-phenanthryl)-propionic acid and β-(10-phenanthryl)-propionic acid have been synthesized and their acid chlorides cyclized.

Three new tetracyclic hydrocarbons, 3,4-cyclopentenophenanthrene, 9,10-cyclopentenophenanthrene and 5,6-benzo-2,3-dihydrobenzonaphthene, have been synthesized.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 30, 1937

[CONTRIBUTION FROM THE PHYSICO CHEMICAL LABORATORY OF THE NEW YORK STATE EXPERIMENT STATION]

The Influence of Neutral Salts on the Optical Rotation of Gelatin. VI. Rotatory Dispersion of Gelatin in Sodium Chloride Solutions[1]

BY D. C. CARPENTER AND F. E. LOVELACE

Publications from this Laboratory[2] have shown that the rotatory dispersion of gelatin was governed by an absorption band at 2200 Å. and that a single term Drude equation $[\alpha]_\lambda = k/(\lambda^2 - \lambda^2_0)$ was adequate to define the dispersion. At 40° the rotatory dispersion constant k was linearly related to the sodium bromide or iodide concentration. At 0.5° the rotatory dispersion was not only affected linearly by the salt concentration, but a new form of gelatin appeared, the amount of which was dependent on the salt concentration according to the equation, $C_{\text{Na halide}} = k \log\left(\frac{a}{1-a}\right) - \log(1/K)$. In these equations the constants have different numerical values for the various sodium halide salts. The value of $k_{0.5°}$ is obviously the sum of the parts contributed by each form of gelatin (k_1 and k_2, having the respective dispersion values 99.54 and 46.33) minus the linear effect of the salt as a solvent medium, $k_{0.5°} = k_1\,(1 - a) + k_2\,(a) - k_0 C_{\text{Na halide}}$. If the two forms of gelatin had different linear salt corrections, each correction factor would have to be introduced in its proper place. In so far as our results go we have found only one such correction factor at 0.5° which seems to apply to both forms at this temperature.

The present paper is a continuation of the rotatory dispersion studies using sodium chloride solutions as solvent and was carried out to ascertain if the above general equations applied to all gelatin-alkali metal halide systems.

Experimental

The procedure for preparing the solutions and for the measurement of rotations, density, *p*H,

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(1) Approved by the Director of the New York State Experiment Station for publication as Journal Paper No. 210.

(2) Carpenter and Lovelace, THIS JOURNAL, **57**, 2342 (1935); **58**, 2438 (1936).

TABLE I

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM CHLORIDE AT 0.5° FOR DIFFERENT WAVE LENGTHS OF LIGHT

				Levo degrees									
				6707.86 Å.		5892.62 Å.		5780.13 Å.		5460.73 Å.		4358.34 Å.	
Soln.	Concn. of NaCl, molal	Density at 25°	*p*H	(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]
1	0.00	1.0023	6.50	3.83	248.01	5.14	332.84	5.38	348.38	6.15	398.24	10.86	703.23
2	.50	1.0232	6.64	3.83	244.45	5.15	328.78	5.39	344.02	6.16	393.16	10.87	693.78
3	1.00	1.0441	6.82	3.86	241.44	5.18	323.99	5.42	339.01	6.20	387.79	10.94	674.27
4	1.50	1.0652	6.81	3.84	235.44	5.16	316.38	5.39	330.48	6.17	378.31	10.89	667.71
5	2.00	1.0866	6.83	3.81	228.98	5.12	307.71	5.36	322.13	6.13	368.42	10.82	650.30
6	2.50	1.1087	6.57	3.74	220.32	5.03	296.32	5.26	309.87	6.02	354.64	10.62	625.61
7	3.00	1.1314	6.42	3.60	207.77	4.83	278.77	5.06	292.04	5.78	333.60	10.21	589.29
8	3.50	1.1545	6.29	3.33	188.35	4.47	252.83	4.68	264.71	5.35	302.60	9.45	534.50
9	4.00	1.1782	6.57	2.93	162.37	3.94	218.35	4.12	228.32	4.72	261.57	8.32	461.07
10	4.20	1.1884	6.17	2.76	151.66	3.70	203.31	3.87	212.65	4.43	243.43	7.81	429.16

TABLE II

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM CHLORIDE AT 40° FOR DIFFERENT WAVE LENGTHS OF LIGHT

				Levo degrees									
				6707.86 Å.		5892.62 Å.		5780.13 Å.		5960.73 Å.		4358.34 Å.	
Soln.	Concn. of NaCl, molal	Density at 25°	*p*H	(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]
1	0.00	1.0023	6.50	1.71	110.73	2.30	148.94	2.41	156.06	2.75	178.07	4.86	314.71
2	.50	1.0232	6.64	1.69	107.86	2.27	144.88	2.37	151.27	2.72	173.60	4.79	305.76
3	1.00	1.0441	6.82	1.68	105.08	2.25	140.73	2.36	147.61	2.70	168.88	4.75	297.10
4	1.50	1.0652	6.81	1.66	101.78	2.23	136.73	2.33	142.86	2.67	163.71	4.71	288.78
5	2.00	1.0866	6.83	1.64	98.565	2.20	132.22	2.31	138.83	2.63	158.07	4.67	280.67
6	2.50	1.1087	6.57	1.62	95.435	2.18	128.42	2.28	134.31	2.61	153.75	4.60	270.99
7	3.00	1.1314	6.42	1.60	92.345	2.15	124.09	2.25	129.86	2.58	148.91	4.55	262.61
8	3.00	1.1545	6.29	1.58	89.367	2.12	119.91	2.22	125.56	2.54	143.66	4.48	253.39
9	4.00	1.1782	6.57	1.56	86.451	2.09	115.82	2.19	121.37	2.50	138.54	4.42	244.94
10	4.20	1.1884	6.17	1.55	85.171	2.08	114.28	2.18	119.79	2.49	136.83	4.40	241.78

etc., was the same as has been described before.[3]

The specific rotation of gelatin in various concentrations of sodium chloride solution was measured at 0.5 and 40° for five different wave lengths of light in the visible spectrum, *viz.*: red lithium line, λ = 6707.86 Å.; sodium D line, λ = 5892.617 Å. (optical mean); yellow mercury line, λ = 5780.13 Å. (optical mean); green mercury line, λ = 5460.73 Å; and the deep blue mercury line, λ = 4358.34 Å. The various light filters employed have been described. The gelatin concentration of the solutions was 0.7656 g. per 100 g. of solution.

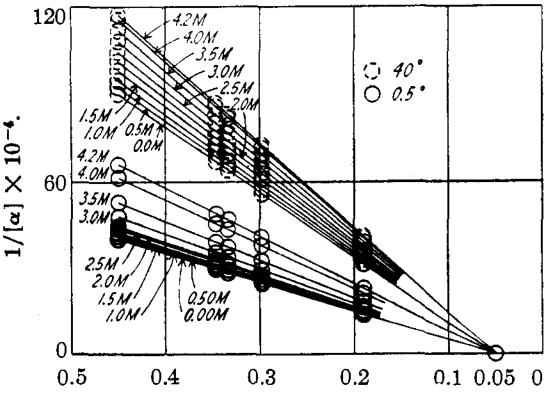

Fig. 1.—Graph of reciprocal of specific rotation *versus* wave length squared at 0.5 and 40°.

Discussion and Conclusions

In Tables I and II are recorded our data for 0.5 and 40°, respectively, for the five wave lengths employed. In Fig. 1 these data are graphed, plotting the reciprocal of specific rotation against the square of the wave length at which the respective rotations were obtained. The relationship is linear, the same as with iodides and bromides, which means that a single-term Drude equation expresses the results.

The straight lines cut the x-axis at λ_0 = 2200 Å. with all of these halides, the location of the absorption band of gelatin. The same value for λ_0 was obtained by solving our data mathematically as was done before. The values of k, numerator in the Drude equation, were calculated for each concentration of sodium chloride and appear in Table III and are graphed in Fig. 2.

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(3) Carpenter, *J. Phys. Chem.*, **31**, 1873 (1927); Carpenter and Kucera, *ibid.*, **35**, 2619 (1931); Carpenter and Lovelace, THIS JOURNAL, **57**, 2337 (1935).

At 40° the k values bear a linear relation to concentration of sodium chloride as given by the equation

$$k_{40°} = 44.517 - 2.458C_{\mathrm{NaCl}} \qquad (1)$$

At 0.5° the curve for the k values is made up of two simultaneously occurring effects, the one a linear relationship to concentration of sodium chloride

$$k_{0.5°} = 99.541 - 2.670C_{\mathrm{NaCl}} \qquad (2)$$

similar to the one above at 40° except for different values for the constants and a second relationship

$$C_{\mathrm{NaCl}} = \frac{1}{0.639} \log \left(\frac{a}{1 - a}\right) - \log (1/K) \qquad (3)$$

where a represents the fraction undergoing change as shown by the change in magnitude of the dispersion constants $k_{0.5°}$. In Table III are given the a values for the fraction undergoing change and the calculated values obtained for log $(1/K)$. The latter agree well with one another and give a mean value of 4.154. The factor 1/0.639 preceding the $[a/(1-a)]$ term regulates how rapidly the change from one form to the other takes place. The ratio between the respective constants for the linear equation $k_{40°}/k_{0.5°}$ for the various halides is 0.92 (sodium iodide), 0.91 (sodium bromide) and 0.92 (sodium chloride), indicating that the salts are affected equally by temperature as might be expected. The actual value of the linear constant seems to be closely related to the molecular weight of the halide, the constant for bromide being about halfway between the constants for chloride and iodide.

TABLE III

ROTATORY DISPERSION CONSTANTS AT 0.5 AND 40°

Soln.	Concn. NaCl, molal	$K_{0.5°}$	a	Log $(1/K)$	$k_{40°}$
1	0.00	99.541	....	...	44.517
2	.50	98.217	....	...	43.293
3	1.00	96.869	....	...	42.132
4	1.50	94.502	0.0195	4.160	40.861
5	2.00	92.000	.0413	4.138	39.594
6	2.50	88.534	.0888	4.147	38.367
7	3.00	83.363	.1537	4.160	37.127
8	3.50	75.611	.2740	4.162	35.869
9	4.00	65.257	.4436	4.156	34.655
10	4.20	60.793	.5174	4.153	34.196

$k_{0.5°} = 99.541 - xC_{\mathrm{NaCl}}$ where $x = 2.670$
$k_{40°} = 44.517 - xC_{\mathrm{NaCl}}$ where $x = 2.458$
Mean log $(1/K) = 4.154$

We have noted before the changes in the value of the $(1/k)$ factor preceding the $[a/(1-a)]$ term and that of the log $(1/K)$ term and that for sodium halides the various log $(1/K)$ terms can be rewritten as a common constant k' log $(1/K)$ of value 2.666, k' being the reciprocal of the former k. The value of the $(1/k)$ factors preceding the $[a/(1-a)]$ term, *i. e.*, 1/0.639, 1/1.33 and 1/2.66 bear a simple relation to one another for the halides, approximately the sixth power of their respective ionic radii as we have pointed out before.

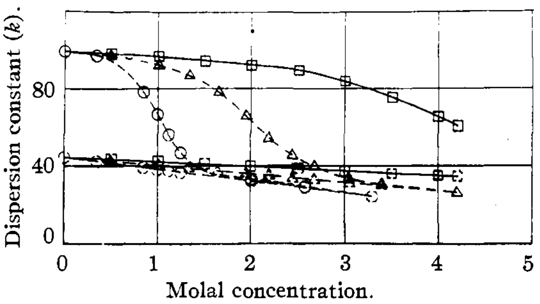

Fig. 2.—Rotatory dispersion constant of gelatin in sodium chloride solutions at 0.5 and 40°: □, NaCl; △, NaBr; ○, NaI.

In Table IV are given the various constants obtained at the various wave lengths for the various combinations employed calculated from the Lucas equation[4] for two optically active molecular species having unequal dispersion constants. The constancy found for a given combination for the five wave lengths used shows that two and only two optically active species of molecule are present, one the original gelatin molecule and the other the molecule after it has undergone the change recorded by the logarithmic equation.

TABLE IV

CALCULATION OF THE LUCAS CONSTANT FOR GELATIN–SODIUM CHLORIDE SYSTEM CONTAINING TWO OPTICALLY ACTIVE COMPONENTS (0.5°)

Combination[a]	6708 Å.	5893 Å.	5780 Å.	5461 Å.	4358 Å.
1-2/1-10	0.0369	0.0313	0.0321	0.0328	0.035
1-3/1-10	.0682	.0683	.0690	.0675	.0702
1-4/1-10	.1304	.1270	.1318	.1287	.1315
1-5/1-10	.1975	.1940	.1933	.1926	.1915
1-6/1-10	.2873	.2819	.2837	.2816	.2832
1-7/1-10	.4176	.4174	.4150	.4175	.4218
1-8/1-10	.6192	.6176	.6163	.6177	.6247
1-9/1-10	.8888	.8834	.8845	.8828	.8966

[a] The numbers in this column refer to corresponding soln. no. in Table I.

In Table V the various dispersion constants found for gelatin–sodium halide systems are summarized.

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[4] Lucas, *Ann. phys.*, **10**, 9, 381 (1928); *Trans. Faraday Soc.*, **26**, 418 (1930).

TABLE V

SUMMARY OF ROTATORY DISPERSION CONSTANTS OF GELATIN IN PRESENCE OF SODIUM HALIDES

	Linear constants		Logarithmic constants	
	$k_{0.5°}$	$k_{40°}$	k	$\log 1/K$
NaCl	2.670	2.458	0.639	4.154
NaBr	4.847	4.415	1.33	2.002
Na I	6.760	6.220	2.66	0.998

Summary

The rotatory dispersion of gelatin in sodium chloride solutions at 0.5 and 40° has been investigated.

At 40° the dispersion constants bear a linear relationship to salt concentration, $k_{40°} = 44.517 - 2.458C_{\text{NaCl}}$.

The dispersion at 0.5° is the result of two effects, one a linear relation to salt concentration $k_{0.5°} = 99.541 - 2.670C_{\text{NaCl}}$, and the other a logarithmic function, $C_{\text{NaCl}} = \frac{1}{0.634}\log\left(\frac{a}{1-a}\right) - \log(1/K)$ in which $\log(1/K)$ equals 4.154.

The various dispersion constants so far found for gelatin-sodium halide systems are summarized.

GENEVA, N. Y. RECEIVED JULY 16, 1937

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE, AND THE UNIVERSITY OF MARYLAND]

Calcium Arsenates. An Investigation into the Three-Component System Calcium Oxide–Arsenic Oxide–Water

BY O. A. NELSON[1] AND M. M. HARING

Approximately 30 million pounds of commercial calcium arsenate is used annually in the United States for combating different types of insects. In spite of this extensive use, however, the knowledge of the chemical and physical characteristics of the basic arsenates of calcium, the only ones suitable for insecticidal purposes, is very limited.

Smith and Murray[2] first showed, by analysis of sixteen brands of commercial arsenates, that the chemical characteristics vary between wide limits. Later Cassil and the senior author,[3a] and also Goodhue,[3b] showed wide variations in both chemical and physical characteristics, from examination of twenty-two brands.

The purpose of the investigation described in this paper was to obtain additional knowledge of the arsenates of calcium through a systematic study of the three-component system calcium oxide–arsenic oxide–water. The plan followed was to make up arbitrary mixtures of the three components, determine the conditions after equilibrium had been reached, and then interpret these from the point of view of the phase rule. The temperature of 62° was chosen, because equilibrium conditions are generally reached in less time at high temperatures and also because most commercial processes for the manufacture of calcium arsenates are carried on at elevated temperatures.

Historical

There are five series of calcium arsenates, distinguished by their molar CaO/As_2O_5 ratio, or acidity. The members of each series differ only in their water content. In the interest of brevity only the formulas and references to original articles are recorded. The numbers in parentheses refer to the relative number of moles of CaO, As_2O_5, and H_2O in the compound. Thus, $Ca(AsO_3)_2$ becomes $1CaO \cdot 1As_2O_5 \cdot 0H_2O$ (1·1·0), while $CaH_4(AsO_4)_2$ becomes $1CaO \cdot 1As_2O_5 \cdot 2H_2O$ (1·1·2).

Compounds with $CaO/As_2O_5 = 1$.

$Ca(AsO_3)_2$ (1·1·0)[4,5,6]
$CaH_4(AsO_4)_2$ (1·1·2)[5,7]
$CaH_4(AsO_4)_2 \cdot H_2O$ (1·1·3)[8]

Compounds with $CaO/As_2O_5 = 2$.

$Ca_2As_2O_7$ (2·1·0)[4,9]
$CaHAsO_4$ or $Ca_2H_2(AsO_4)_2$ (2·1·1)[10]
$CaHAsO_4 \cdot H_2O$ (2·1·3)[5,7,10,11,12]
$CaHAsO_4 \cdot 2H_2O$ (2·1·5)[6,12-15]
$CaHAsO_4 \cdot 3H_2O$ (2·1·7)[6]

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(1) Abstracted from a dissertation presented by the senior author to the faculty of the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

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(3) (a) O. A. Nelson and C. C. Cassil, *J. Econ. Ent.*, **30**, 474–478 (1937); (b) L. D. Goodhue, *ibid.*, **30**, 466–474 (1937).

(4) C. L. Bloxam, *Chem. News*, **54**, 193–194 (1886).

(5) P. Kotschoubey, *J. prakt. Chem.*, **49**, 182–190 (1850).

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(10) H. Debray, *ibid.*, [3] **61**, 419–455 (1861).

(11) H. Goguel, *Mem. soc. sci. phys. Nat. Bordeaux* [5] **1**, 85 (1896).

(12) W. Haidinger, *Edinburgh J. Sci.*, **3**, 302–306 (1825).

(13) E. Turner, *ibid.*, **3**, 306–310 (1825).

(14) H. Dufet, *Compt. rend.*, **106**, 1238–1240 (1888).

(15) A. de Schulten, *Bull. soc. franç. mineral.*, **26**, 18–24 (1903).