(72%) of trichloroethyl acetate, b.p. 62° (13 mm.), was obtained. *Anal.* Calcd. for $C_4H_5O_2Cl_3$: C, 25.09; H, 2.63; Cl, 55.56. Found: C, 24.94; H, 2.57; Cl, 56.31.

Similarly trichloroethyl 3,5-dinitrobenzoate, m.p. 142–143°, was prepared in 81% yield in carbon tetrachloride within an hour. The quantity of aluminum chloride used was 30% of the molar quantities of the reactants. A control experiment was made at the same time in which no aluminum chloride was used. No reaction was observed and a quantitative recovery of the acid chloride was made. *Anal.* Calcd. for $C_9H_5O_6N_2Cl_3$: C, 31.46; H, 1.47; N, 8.15; Cl, 30.96. Found: C, 31.25; H, 1.44; N, 8.09; Cl, 30.43.

With aluminum bromide as catalyst, β,β,β-tribromoethyl benzoate, m.p. 38°, and β,β,β-tribromoethyl 3,5-dinitrobenzoate, m.p. 164–165°, were easily prepared in 80–90% yields in carbon tetrachloride. These esters do not appear to have been reported previously. *Anal.* Calcd. for $C_9H_7O_2Br_3$: Br, 61.97. Found: Br, 61.80. Calcd. for $C_9H_5O_6N_2Br_3$: Br, 50.27. Found: Br, 50.92.

The use of aluminum chloride in the esterification of an ordinary alcohol and acid chloride was first reported by Combes,[3] who isolated an acetyl chloride–aluminum chloride complex and poured it into cold ethanol. The resulting energetic reaction gave a mixture of several products. However, our work indicates that the application of metal halide catalysts to esterifying unreactive alcohols and acid chlorides in the manner outlined above gives good yields of esters. Investigation is being continued in exploring the applicability of the method and the relative efficiency of various Friedel–Crafts type catalysts.

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Detection of Some Unknown Porphyrin Products Related to Deuteroporphyrin IX by Paper Chromatography[1]

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In the course of preparing deuteroporphyrin IX dimethyl ester[2] from red blood cells and resorcinol, several unknown porphyrin products have been detected by paper chromatography.[3] This paper reports the separation of these compounds and a study of their properties.

TABLE I

SOME PHYSICAL PROPERTIES OF THE PORPHYRIN PRODUCTS

	$R_f^{23^\circ}$ (free/ester)		Absorptions, mμ (methyl ester)									HCl no.[a]		Yield,[d]
	KC–KP[b]	KCP[c]	Organic solvents: (E), ether; (EA), ethyl acetate						Acid soln. (HA)–HOAc, (%)–%HCl			Free	Ester	%
R₁[e]	0.50/0.91	0.40/0.92	(E)	622	597	569	526	498–94	(5%)	590	547	0.4	1.5	74
			(EA)	621	596	568	527	498						
R₂	.30/ .50	0 / .49	(E)	624	596	570	530	499	(HA + 10%)	593	550	.4	1.5	19
			(EA)	623	595	569	532	499						
R₃	.30/ .50	0 / .63	(E)	625	596	570	534	500		...		...	...	1
R₄	0 / .35	0 / .08	(E)	627	600	572	533	500	(HA + 25%)	598	555	.9	1.2	5
			(EA)	625	599	569	534	502						
R₅	0 / .35	0 / .17	(E)	628	602	572	535	501	(HA + 25%)	598	555	1.0	1.8	0.5
			(EA)	626	599	569	535	502						
R₆	.. / .59	.. / .69	(E)	623	596	566	526	496		...		...	2.5	..
			(EA)	622	595	568	529	500						
CuR₂	....	....	(EA)	560	525				(HA)	562	527	...	...	..

[a] The concentration in % of HCl which will extract $^2/_3$ of the porphyrin from an equal volume of ether solution. [b] Kerosene, chloroform–kerosene, *n*-propyl alcohol solvent system.[3] [c] Kerosene, chloroform, *n*-propyl alcohol system.[2] [d] Relative yield of the products, based on fluorescence measurements from a typical preparation from RBC. [e] Deuteroporphyrin IX.

Experimental

(I) Preparation and Separation.—The method of preparation of deuteroporphyrin IX dimethyl ester and the presence of other porphyrins in the crude product were described in a previous paper.[2] When the crude product was chromatographed on a $CaCO_3$ column with a mixture of ethyl acetate and benzene (1:12), the porphyrin esters separated into three red fluorescent zones under ultraviolet light. The lowest main zone R_1 was identified as deuteroporphyrin IX dimethyl ester. The other two zones as shown by paper chromatography were still mixtures. Repeated secondary chromatography with the same solvent system (1:10) resolved the middle zone into R_2 and a less adsorbed minor component R_3, and the top zone with the solvent system (1:8) into R_4 and another less adsorbed minor component R_5. The paper chromatographic R_f values for both the free porphyrins and esters in different solvent systems are listed in Table I.

(II) Properties.—Due to the extremely small quantities isolated these porphyrin products were not obtained in crystalline form. Although attempt was made to crystallize R_2 from different solvents even under solid CO_2 cooling or vacuum drying for many months, no crystals were obtained and its copper complex was also not crystalline. However, R_2 could be precipitated by CCl_4 from ethyl acetate solution. The properties of R_2 and other members were studied on the chromatographically pure products. In general they are quite stable in most organic solvents and fairly so in acid, but very unstable in alkaline solutions.

(A) Absorption Spectra.—Absorption experiments were done with a Beckman DU spectrophotometer.[4] Its cell compartment has been equipped with a thermostatically controlled device to minimize the change of sample concentration. For comparison, their fluorescence intensities have been taken as a measure of concentration, with 2 γ coproporphyrin I in 10 ml. of 1% HCl solution as a standard. The measurements were made against the solvent at 25°. The spectra of pure crystalline dimethyl esters of deuteroporphyrin IX and protoporphyrin IX were also measured for reference (Fig. 1). The strong Soret band of each of them in the near ultraviolet region was observed but not measured.

(B) Fluorescence—*p*H Curve.—The relation between *p*H and the fluorescent property of these porphyrins was studied on a Coleman 14 universal spectrophotometer with the fluorescence attachment. Stock solutions were prepared from samples of known fluorescence intensity in ethyl acetate solution. Each vacuum-dried sample was dissolved

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(1) This investigation was supported by a research grant from The National Institutes of Health, Public Health Service.

(2) T. C. Chu and E. J.-H. Chu, THIS JOURNAL, **74**, 6276 (1952).

(3) T. C. Chu, A. A. Green and E. J.-H. Chu, *J. Biol. Chem.*, **190**, 643 (1951).

(4) The authors are indebted to Dr. T. M. Doscher and Mr. J. Myer of The University of Southern California for using the instrument.

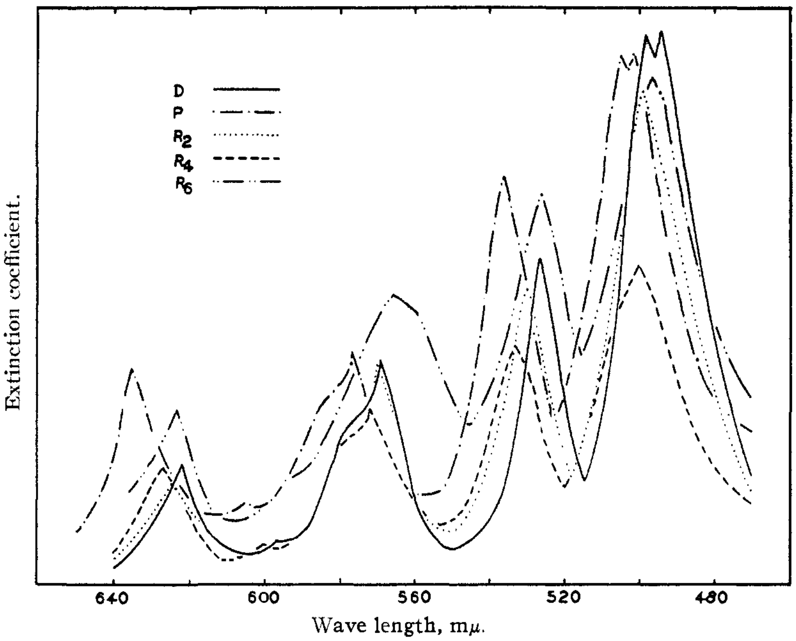

Fig. 1.—The absorption spectra of methyl esters of deuteroporphyrin IX (D), protoporphyrin IX (P), R_2, R_4 and R_6 in ether.

in calculated amounts of 5% HCl containing 5% acetic acid to a final concentration of "2 γ" per ml. in coproporphyrin I units. The solution was allowed to stand for 24 hours for complete hydrolysis. For each determination, 1 ml. of the stock solution was generally mixed with 9 ml. of sodium citrate buffer or HCl or NaOH of proper concentration as the case might be. In the *p*H region, the final *p*H of each solution after fluorescence measurement was determined in a Beckman G *p*H-meter. The curves for deutero- and protoporphyrin IX were also included in Fig. 2, but with 0.5-ml. samples.

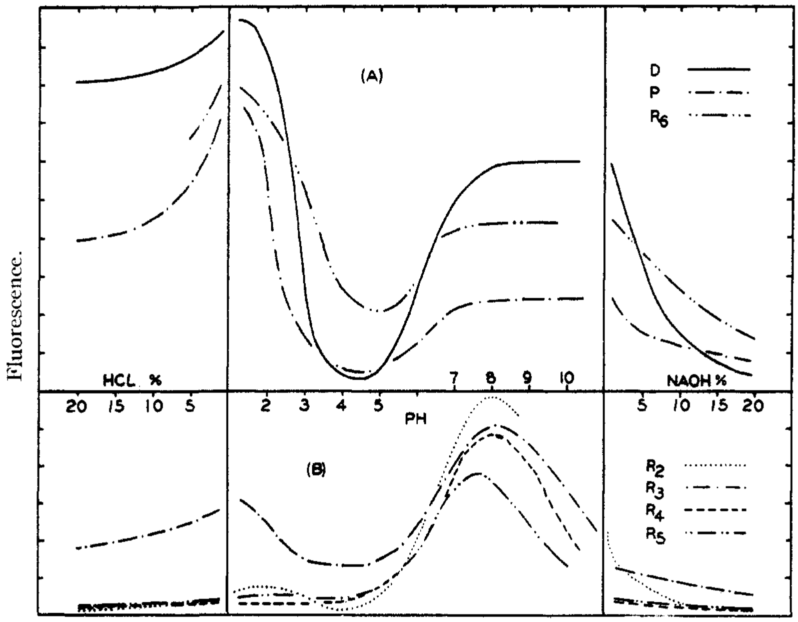

Fig. 2.—Fluorescence-*p*H curves of deuteroporphyrin IX (D), protoporphyrin IX (P), R_2, R_3, R_4, R_5 and R_6.

It has been observed that deuteroporphyrin, protoporphyrin, etc. (Fig. 2A), decreased their fluorescence values gradually on standing in strong alkaline solutions while other porphyrins (Fig. 2B) showed a tendency to increase. On the other hand, between *p*H 6–11 the latter group revealed a tendency to decrease their intensity while the former group was quite steady.

Analyses of the products recovered from these experiments by paper chromatography showed that the compounds of group (2B) had undergone some sort of change mainly into non-fluorescent substances and partly to other porphyrins including deuteroporphyrin. In the buffer solution of *p*H 6–11, more non-fluorescent products were formed.

(C) Reaction with NaOH.—When a solution of "5 γ" R_2 in 10 ml. of 4% NaOH was irradiated in the Coleman, the intensity of fluorescence increased to a maximum in about 20 minutes, then decreased slowly and smoothly for about an hour to reach its half value. Neither 1 nor 10% NaOH was as effective as the 4% solution. Paper chromatographic analysis of the reacting mixture at various stages showed that (1) at the glowing stages, a new porphyrin designated hereafter as R_6 and deuteroporphyrin were formed (2:1) increasingly at the expense of R_2; (2) at the declining stages, no R_2 but reducing amounts of R_6 and deuteroporphyrin were found. The reaction between R_2 and NaOH took place even in the dark and under nitrogen atmosphere but at much slower rate. Meanwhile, the addition of an equal volume of 30% H_2O_2 to 4% NaOH solution of R_2 gave essentially the same result. It seems that the reaction is independent of any mild oxidizing agent.

In reaction with NaOH, R_3 gave rise to R_6 and deuteroporphyrin, whereas R_4 gave R_6 as the main porphyrin product and R_5 gave R_2, R_3 and R_6, but with even poorer yields in all cases.

(D) Isolation of R_6 and Chromatographic Roll.—When protoporphyrin IX dimethyl ester was used instead of red blood cells in the fusion mixture, more R_2 resulted. A total of "2200 γ" (copro-I units) of chromatographically pure R_2 was obtained from 25 mg. of protoporphyrin ester. R_3, R_4 and R_5 were also found together with some deuteroporphyrin.

For the preparation of R_6, larger quantities of R_2 were treated with 4% NaOH in a beaker under sunlight. A pilot sample was placed in the Coleman beforehand in order to find out the possible maximum intensity. After 5 minutes testing, samples were taken at short intervals to determine the right time of exposure. For instance, under the hazy Los Angeles sunshine in May, it took 7–8 minutes. The reaction mixture was then immediately neutralized with 15% HCl, extracted and esterified as usual. The separation was effected by means of a chromatographic roll. It was made by rolling a sheet of Whatman No. 1 paper (15 × 57 cm.) into a doubly coiled No. 16 nichrome wire frame. Instead of spotting, a sample was applied all along the basal line 2 cm. from the bottom. The roll was developed in a 2-l. beaker containing 20 ml. of kerosene–chloroform (1:1) for about 40 minutes. The compound R_6 appeared in the middle of the papergram as a clear band with deuteroporphyrin band almost at the top and the residual R_2 at the bottom. Several minor products of the reaction which were not shown in the spot papergram were thus detected as faint bands between main ones. These bands were cut out from the dried papergram along pencil tracings made under ultraviolet light, and extracted with ethyl acetate. An average yield of "3 γ" of R_6 was obtained from "100 γ" of R_2.

As far as the fluorescence property is concerned, R_6 resembles deuteroporphyrin more than R_2, R_3, etc. In NaOH solution, its fluorescence disappears almost at the same rate as that of deuteroporphyrin; but in organic solvents it is not as thermostable as that of the latter. For instance, it loses its fluorescence considerably even at 105°. R_3 is also very unstable around this temperature, changing partly into the more stable R_2.

HCl numbers of these products and absorption data of the copper complex of R_2 ester are listed together in Table I.

Discussion

The absorption data of these porphyrin products indicate the absence of vinyl groups. This point has been supplemented by the negative qualitative test for the vinyl group.[5] Although R_2 is most probably an intermediate in the formation of deuteroporphyrin, it is not 4-vinyldeuteroporphyrin,[6] spirographisporphyrin,[7] monoformyl or diformyl deuteroporphyrin,[8] as evidenced by the spectroscopic data and negative chemical tests toward the reagents, diazoacetic methyl ester and hydroxylamine.

The different trends noted in the fluorescence changes of the group (Fig. 2B) are shown by the NaOH reaction. With a 4% NaOH, they give R_6 and deuteroporphyrin as the main fluorescent products. As shown in Fig. 2A, these porphyrins have more intense fluorescence in the strongly alkaline region. On the other hand a reacting medium with *p*H between 6–11 is favorable for the formation of non-fluorescent products.

The results of the NaOH reaction which may be outlined as $R_5 \rightarrow R_2(R_3) \rightarrow R_6 +$ deutero, support the view that they are most likely the precursors of deuteroporphyrin IX and should play some roles in the mechanism of the formation of deuteroporphyrin by the resorcinol fusion.

The authors wish to express their appreciation to Sister Agnes Ann Green for her interest in the work.

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Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Stannic and Stannous Sulfides

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Existing thermodynamic information on the sulfides of tin is rather meager, and low-temperature heat-capacity and entropy data have been entirely lacking. This paper presents the results of low-temperature heat capacity measurements of both stannic and stannous sulfides, with an evaluation of their entropies at 298.16°K.

Materials.—The stannic sulfide was prepared by K. R. Bonnickson of this Laboratory from reagent-grade stannous chloride dihydrate, sulfur and ammonium chloride. These ingredients were mixed in the molal proportion of 1:3:2 and heated in an open-end tube, first at 150° until evolution of water ceased and then for three hours at 300–350°, after which the tube was stoppered and cooled. The reaction mass was broken up, shaken with water, and centrifuged four times. It was then shaken with alcohol, centrifuged and dried at 60°. Finally the product was mixed with 10% by weight of sulfur and heated in vacuum for five hours at 300°, the excess sulfur being distilled off in the process. The product analyzed 64.95% tin, as compared with the theoretical 64.92%. The X-ray diffraction pattern agreed with that given for stannic sulfide in the A.S.T.M. catalog, except for the presence of four weak lines that could not be identified.

The stannous sulfide was furnished by M. J. Spendlove of the College Park, Md., Station of the Bureau of Mines. It was prepared by adding sulfur to an excess of molten tin, skimming off the reaction product, and roasting at 980° to remove excess sulfur and produce a crude grade of stannous sulfide. The crude material then was purified by sublimation in vacuum, which gave a well crystallized, dense product. Chemical analysis showed the substance to contain 99.2% stannous sulfide and 0.6% stannic oxide, leaving about 0.2% unaccounted for. Spectrographic analysis indicated less than 0.01% each of aluminum, bismuth, iron, magnesium, calcium, sodium and copper, while silicon and lead may run as high as 0.05%.

Measurements and Results.—The measurements were conducted with previously described apparatus.[1] The sample masses employed were 104.12 g. of stannic sulfide and 338.98 g. of stannous sulfide. The stannous sulfide results were corrected for the 0.6% stannic oxide content by means of the heat capacity data of Millar,[2] the correction ranging from 0.38% at the lowest temperature to zero at the highest. No correction of the stannic sulfide results was necessary.

The measured heat capacities appear in Table I, being expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole. Molecular weights accord with the 1951 International Atomic Weights.[3]

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
SnS_2 (mol. wt., 182.83)					
52.75	4.139	114.65	10.24	216.55	15.16
56.45	4.453	124.72	11.02	226.55	15.38
60.65	4.874	135.98	11.80	236.88	15.62
65.17	5.389	146.13	12.43	246.21	15.84
70.05	5.900	155.79	12.92	257.06	16.02
74.92	6.407	166.54	13.44	266.82	16.21
80.28	6.976	176.14	13.85	276.28	16.39
84.04	7.387	186.22	14.24	287.38	16.58
93.66	8.356	196.28	14.56	296.54	16.76
105.07	9.435	206.63	14.87	(298.16)	(16.76)
SnS (mol. wt., 150.77)					
52.45	4.762	114.70	8.837	216.37	11.10
56.82	5.115	125.28	9.249	226.05	11.19
61.40	5.525	136.01	9.607	236.31	11.28
65.90	5.920	146.22	9.901	246.03	11.37
70.49	6.277	155.93	10.13	256.19	11.45
75.28	6.623	166.03	10.34	266.05	11.55
80.20	6.974	176.12	10.54	276.36	11.61
83.71	7.208	186.09	10.69	286.68	11.69
94.67	7.868	195.91	10.84	296.80	11.77
104.47	8.368	206.31	10.95	(298.16)	(11.77)

Both substances exhibit normal heat capacity curves. The only unusual feature is that, at tem-

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