ether, of the nitrourethans, and acidification of the resulting ammonium salts. Nitrourethan was prepared by a slight modification of the direct nitration of Brian and Lamberton[8] in which the nitration mixture was drowned in ice-water and then ether-extracted directly to give a 97% yield of product.

Ethylenedinitramine, (EDNA), was prepared from 2-imidazolidone according to the directions of Bachmann, *et al.*[3b]

2,4-Dinitro-2,4-diazapentane (I). (A).—To a solution of 2.5 g. of paraformaldehyde in 160 ml. of 90% (by weight) sulfuric acid, chilled in an ice–salt-bath (−2 to −6°), was added, in small portions and with vigorous stirring, 9.0 g. of methylnitramine. The solution was stirred about 10 minutes after the addition and was then poured onto a large quantity of ice. On standing 1.7 g. of material, m.p. 41–44°, slowly precipitated. Ether extraction of the filtrate gave a further 2.1 g. of product melting at 48–50.8°. These combined products represent a 39% yield. By recrystallization from a chloroform–hexane mixture an analytical sample, melting at 49.2–50.9°, was realized.

Anal. Calcd. for $C_3H_8N_4O_4$: C, 21.95; H, 4.91; N, 34.14. Found: C, 22.11, 21.92; H, 4.86, 4.79; N, 33.99.

(B).—A mixture of 1.5 g. of methylnitramine, 0.4 g. of paraformaldehyde, 16 ml. of trifluoroacetic anhydride and 10 drops of boron trifluoride etherate was stirred 2.5 hours with ice-bath cooling. After standing overnight in the refrigerator the mixture was poured onto ice, neutralized with sodium bicarbonate and ether extracted. The ether was dried over magnesium sulfate and was evaporated, leaving 0.3 g. of a brown oil which could not be induced to crystallize. The oil was dissolved in 10 ml. of chloroform, poured onto a one cm. (10 g.) column of activated alumina, and eluted with 40 ml. of chloroform. The eluate solidified on long standing.

Anal. Calcd. for $C_3H_8N_4O_4$: N, 34.14. Found: N, 33.97.

On recrystallization from chloroform–hexane the melting point was 49–51° and there was no melting point depression when mixed with the material from method (A).

3,5-Dinitro-3,5-diazaheptane (II).—To a solution of 0.7 g. of paraformaldehyde in 50 ml. of 90% sulfuric acid was added 3.0 g. of ethylnitramine as in method (A) for compound I. The drowned reaction mixture deposited 1.7 g. of a white solid melting at 74–77° and ether extraction of the filtrate gave 0.2 g. of solid for a total yield of 43%. An analytical sample, m.p. 75.7–77.2°, was realized by crystallization from hexane.

Anal. Calcd. for $C_5H_{12}N_4O_4$: C, 31.25; H, 6.30; N, 29.15. Found: C, 31.24, 31.31; H, 6.35, 6.28; N, 29.36, 29.48.

5,7-Dinitro-5,7-diazaundecane (III). (A).—Over a 40-minute period 8.4 g. of *n*-butylnitramine was added to a solution of 4.0 g. of paraformaldehyde in 150 ml. of 82.5% sulfuric acid according to the conditions for compound I. The drowned reaction mixture precipitated 4.2 g. of product melting at 65–70°. This constitutes a 48% yield. Use of 74% sulfuric acid gave a 13% yield of the condensation product. One recrystallization from hexane gave the analytical sample melting at 72–73.5°.

Anal. Calcd. for $C_9H_{20}N_4O_4$: C, 43.54; H, 8.12; N, 22.57. Found: C, 43.32; H, 8.00; N, 22.44.

(B).—A mixture of 1.6 g. of *n*-butylnitramine, 50 ml. of dry ether, 1.0 g. of paraformaldehyde and 5 ml. of boron trifluoride etherate was refluxed for 8 hours, giving a clear solution. This was washed with 5 portions of water, dried with magnesium sulfate, and evaporated to give a small amount (*ca.* 0.2 g.) of a brown oil which, taken up in hexane and chilled, deposited a white solid, m.p. 72–73.5°, which gave no melting point depression when mixed with the material from method (A).

1,3-Dinitro-1,3-diazacyclopentane (IV). (A).—To a solution of 1.2 g. of paraformaldehyde in 50 ml. of 87% sulfuric acid was added 3.0 g. of EDNA according to the conditions for compound I. The drowned reaction mixture gave 1.8 g. of a white solid melting at 95–115°. This was added to 10 ml. of commercial 100% nitric acid chilled in an ice–salt bath, let stand 10 minutes, and poured onto ice to give 0.9 g. (28% yield) of a white solid melting at 128.5–133.5° (softening at 122°). Recrystallization from 50 ml. of 95% ethanol gave 0.6 g. of product melting at 132.5–134°.

(B).—To 58 ml. of 89% sulfuric acid, chilled in an ice–salt bath, was added 6.8 g. of N-methylol EDNA[3] over a period of 20 minutes. After 20 minutes of additional stirring the viscous mixture was poured onto an excess of ice to give 5.2 g. (85% yield) of product melting at 132.5–134°. This was recrystallized from 95% ethanol (50 ml./g.) to give an analytical sample melting at 132.5–133.5°.

Anal. Calcd. for $C_3H_6N_4O_4$: H, 3.73; N, 34.56. Found: H, 3.72, 3.92; N, 34.30, 34.49.

N-Methylol EDNA was recovered unchanged after being stirred for several hours at room temperature in trifluoroacetic anhydride containing a catalytic amount of boron trifluoride etherate.

Attempted Condensations with Other Primary N-Nitro Compounds.—The use of nitrourethan with solutions of paraformaldehyde in 80 to 90% sulfuric acid gave only water soluble products on drowning. Ether extraction of the aqueous solutions gave nitrourethan, identified by mixed melting point with the starting material.

The addition of cyclohexylnitramine to a solution of paraformaldehyde in 90% sulfuric acid gave a small amount of non-crystallizable yellow oil which could not be separated into recognizable products. The use of 75% sulfuric acid gave about 50% recovery of the starting nitramine and no other identifiable products.

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(8) R. C. Brian and A. H. Lamberton, *J. Chem. Soc.*, 1633 (1949).

Esterification Catalysis by Metal Halides

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We have found that Friedel–Crafts type catalysts are very effective for accelerating the rate of reaction at low temperature between acid chlorides and polar alcohols, such as 2,2,2-trichloroethanol and 2,2,2-tribromoethanol. Anhydrous aluminum chloride is most active and ferric chloride, titanium tetrachloride, antimony pentachloride, boron fluoride, stannic chloride, zinc chloride and mercuric chloride are also useful in varying degree.

Examples of the catalytic effect of aluminum chloride are the preparations of β,β,β-trichloroethyl acetate and β,β,β-trichloroethyl 3,5-dinitrobenzoate. β,β,β-Trichloroethyl acetate has previously been prepared from acetyl chloride and trichloroethanol by methods requiring high temperature and long reaction periods.[1,2] The use of anhydrous aluminum chloride permits this reaction to occur easily in a solvent at low temperature.

At room temperature 1.56 g. (0.020 mole) of acetyl chloride and 3.00 g. (0.020 mole) of trichloroethanol were dissolved in 5 ml. of chloroform. Very little reaction was observed. The addition of 0.13 g. (0.001 mole) of crushed anhydrous aluminum chloride caused a vigorous exothermic reaction with copious evolution of hydrogen chloride gas. After five minutes 0.39 g. (0.003 mole) of additional aluminum chloride was added and the reaction continued vigorously for 10 minutes and then subsided. Warming to 45° completed the reaction in 20 minutes. The chloroform was evaporated and the residue treated with ice-cold dilute hydrochloric acid, extracted with ether, and distilled under vacuum after removal of the ether. A yield of 2.75 g.

(1) R. Nakai, *Biochem. Z.*, **152**, 272 (1924).
(2) K. Garsarolli-Thurnlackh, *Ann.*, **210**, 63 (1881).

(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 $C_9H_5O_8N_2Cl_3$: 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.

(3) A. Combes, *Compt. rend.*, **103**, 814 (1887).

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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.

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

TABLE I

SOME PHYSICAL PROPERTIES OF THE PORPHYRIN PRODUCTS

	$R_f^{23°}$ (free/ester) KC–KP[b]	$R_f^{23°}$ (free/ester) KCP[c]	Absorptions, mμ (methyl ester) Organic solvents: (E), ether; (EA), ethyl acetate						Acid soln. (HA)–HOAc, (%)–%HCl			HCl no.[a] Free	HCl no.[a] Ester	Yield,[d] %
R_1[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						
R_2	.30/ .50	0 / .49	(E)	624	596	570	530	499	(HA +	593	550	.4	1.5	19
			(EA)	623	595	569	532	499	10%)					
R_3	.30/ .50	0 / .63	(E)	625	596	570	534	500		...		...	...	1
R_4	0 / .35	0 / .08	(E)	627	600	572	533	500	(HA +	598	555	.9	1.2	5
			(EA)	625	599	569	534	502	25%)					
R_5	0 / .35	0 / .17	(E)	628	602	572	535	501	(HA +	598	555	1.0	1.8	0.5
			(EA)	626	599	569	535	502	25%)					
R_6	.. / .59	.. / .69	(E)	623	596	566	526	496		...		...	2.5	..
			(EA)	622	595	568	529	500						
CuR_2	.....	.....	(EA)	560	525				(HA)	562	527	...	...	..

[a] The concentration in % of HCl which will extract ⅔ 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.

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(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).

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