method of Gilman and Nelson.[5] The reaction mixture was then refluxed gently for four hours during which time a grayish, sirupy precipitate was formed. The reaction mixture was cooled with an ice-bath and hydrolyzed carefully with 180 ml. of 20% sulfuric acid. The ether layer was separated and combined with an ether washing of the water layer. The ethereal solution was then extracted twice with 50 ml. of 10% potassium carbonate solution.

The carbonate solution was filtered and carefully acidified with dilute sulfuric acid. A 3-acetamino-acetylbenzoic acid was precipitated along with some brownish gummy substance. This was filtered and the filtrate extracted twice with a small amount of ether. Some more of the acid was obtained on evaporating the ether solution. The combined crude product thus obtained was recrystallized from a water–alcohol mixture, yield, 0.75 g. (6.5%) of colorless, transparent crystals; m. p. 142.5–144°.

Anal. Calcd. for $C_{11}H_{11}NO_4$: neut. equiv., 221; C, 59.70; H, 4.98; N, 6.33. Found: neut. equiv., 220; C, 59.80; H, 5.10; N, 6.13.

The potassium carbonate extracted ethereal solution was evaporated to dryness and a colorless solid was obtained. The substance after recrystallization from alcohol was identified as 4-acetamino-3,3-dimethylphthalide; yield, 2.60 g. (22%); m. p. 127.5°.

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.93; N, 6.40. Found: C, 65.68; H, 6.08; N, 6.19.

4-Amino-3,3-dimethylphthalide.—One gram of 4-acetamino-3,3-dimethylphthalide was refluxed with 15 ml. of 0.6 *N* alcoholic potash solution for an hour. The reaction mixture was evaporated, acidified with dilute hydrochloric acid and extracted with ether to remove any acidic substance. The water layer was then converted again to the alkaline side with dilute sodium hydroxide and extracted twice with a small amount of ether. The combined ether extract was evaporated and the residue recrystallized twice from alcohol. The colorless plates thus obtained were 4-amino-3,3-dimethylphthalide, m. p. 70°; yield, 0.7 g. (87%).

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.22; N, 7.91. Found: C, 67.58; H, 6.18; N, 7.99.

3,3-Dimethylphthalide.—Phthalic anhydride (9.9 g., 0.067 mole) was treated with an ethereal solution of dimethylcadmium prepared from 8.9 g. (0.37 mole) of magnesium, 50 g. (0.53 mole) of methyl bromide, 39 g. (0.21 mole) of cadmium chloride and 300 ml. of dry ether according to the method of Gilman and Nelson.[5] The reaction mixture was refluxed for two hours, cooled and hydrolyzed with 215 ml. of 20% sulfuric acid. The ether layer was separated and combined with an ether washing of the water layer. The ethereal solution was extracted twice with 50 ml. of 10% potassium carbonate solution. The carbonate extracted ethereal solution was evaporated and the residue recrystallized from alcohol; 6.5 g. (60%) of 3,3-dimethylphthalide were obtained, m. p. 67.5°.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.07; H, 6.17. Found: C, 74.26; H, 6.18.

The carbonate extract was acidified with dilute sulfuric acid. A very small amount of 2-acetylbenzoic acid was recovered.

Anal. Calcd. for $C_9H_7ClO_2$: Cl, 19.45. Found: Cl, 18.95.

Summary

3,3-Dimethylphthalide and its 4-amino-4-acetamino and 4-nitro derivatives were prepared from phthalic anhydride. Studies of the preparation and reduction of 2-acetyl-3-nitrobenzoic acid were made.

CORVALLIS, OREGON RECEIVED FEBRUARY 6, 1947

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,[1] PHILADELPHIA 18, PA.]

Preparation of N,N-Dimethylacrylamide by Pyrolysis of N,N-Dimethyl-α-Acetoxypropionamide

BY W. P. RATCHFORD AND C. H. FISHER

Acrylamides, which are similar to acrylic acid and acrylic esters[2] in being capable of addition polymerization,[3,4,5] have been made by the reaction of acrylyl chloride with ammonia or amines,[3,5,6,7] removal of hydrogen chloride from β-chloro-propionamides,[8,9] interaction of N,N-diethyl-α-bromopropionamide with Grignard reagents,[10] decomposition of β-dimethylaminopropionamide,[11] and the interaction of acetylene, carbon monoxide and amines.[12] Acrylamides cannot be made satisfactorily by treating methyl or ethyl acrylate with amines because primary and secondary amines add readily to the olefinic linkage of acrylic esters.[13]

The primary purpose of the present work was to develop a convenient and inexpensive method for transforming lactic acid into N,N-dimethylacryl-

$$\underset{\text{I}}{CH_3COOCH(CH_3)CON(CH_3)_2} \longrightarrow \underset{\text{II}}{CH_2{=}CHCON(CH_3)_2} + CH_3COOH$$

$$\underset{\text{III}}{CH_3COOCH(CH_3)COOCH_3} \longrightarrow \underset{\text{IV}}{CH_2{=}CHCOOCH_3} + CH_3COOH$$

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

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[13] D. R. Howton, *J. Org. Chem.*, **10**, 277 (1945); K. Morsch, *Monatsh.*, **63**, 220 (1933); R. Mozingo and J. H. McCracken, "Organic Syntheses," **20**, 35 (1940); and E. Philippi and E. Galter, *Monatsh.*, **51**, 253 (1929).

TABLE I

PYROLYSIS OF N,N-DIMETHYL-ALPHA-ACETOXYPROPIONAMIDE

Expt.	Pyrolyzed, g.	Temp., °C.	Contact time, sec.[a]	Pyrolysis rate, mole/hr.	Liquid pyrolyzate %	Liquid pyrolyzate *N* NaOH to neutralize 1 g., ml.	Acetoxy amide recovered, %	Yield, % of theoretical[b] Alkyl acrylamide[c]	Yield, % of theoretical[b] Acetic acid Titration	Yield, % of theoretical[b] Acetic acid Distillation
1	104.8	500	2.9	0.507	99.2	3.53	40	82	93	60
2	138.8	559	1.9	.536	96.5	5.79	4	89	92	57
3	133.3	557	2.4	.514	96.7	5.82	0	93	89	57
4	334.2	532	2.9	.504	97.9	5.24	0[d]	96	101	66
5	293.7	532	3.8	.385	98	5.25	0[d]	94	98	56
6	235	523	2.6	.504	98.7	4.78	0[d]	99	101	67
7	769	521	3.0	.452	97.9	4.88	21.5	87	99.5	57
8	2616	520	2.7	.514	97.5	4.61	28	88	98	61.5

[a] Based on the free space in the pyrolysis tube within 15° of the stated pyrolysis temperature. [b] On the basis of unrecovered acetoxy amide. [c] Corrected for acetic acid present (approximately 15% by weight). [d] Acetoxy amide may have been present in high boiling fractions, but it was not detected.

amide (II), a useful chemical and resin intermediate. Another purpose was to compare the pyrolysis behavior of N,N-dimethyl-α-acetoxypropionamide on pyrolysis (I) with that of its oxygen-analog (methyl-α-acetoxypropionate (III)), which decomposes[14,15] into methyl acrylate and acetic acid.

N,N-Dimethyllactamide was made conveniently and in high yield by allowing methyl lactate to react with dimethylamine at room temperature. The dimethyllactamide was acetylated with acetic anhydride, acetic acid, vinyl acetate or ketene. Acetic anhydride appeared most suitable for the laboratory acetylation of the hydroxy amide, a 97% yield of N,N-dimethylacetoxypropionamide (I) being easily obtained.

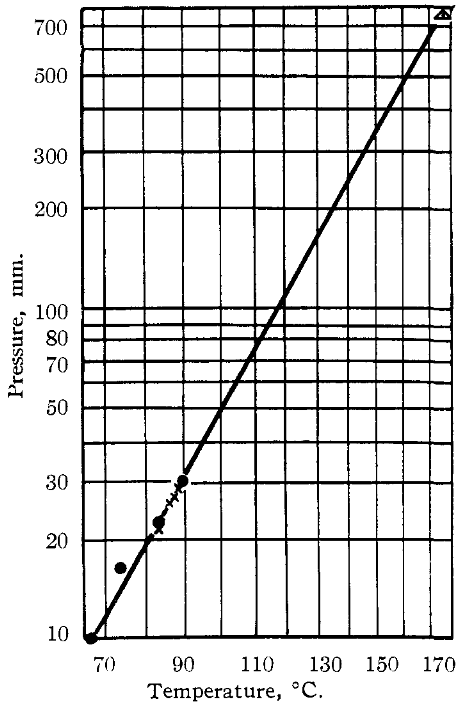

Fig. 1.—Boiling point of N,N-dimethylacrylamide (prepared by pyrolysis, ●; from acrylyl chloride, ×; N,N-dimethylpropionamide, ⚠).

The saponification equivalents of the acetoxypropionamide (I) indicate that the ester and amide groups differ markedly in ease of saponification. Hydrolysis of the ester group in alcoholic alkali was virtually complete, but the amide group was unaffected under the conditions used.

Under conditions suitable for converting methyl acetoxypropionate into methyl acrylate (500–560°), N,N-dimethylacetoxypropionamide decomposed satisfactorily into N,N-dimethylacrylamide and acetic acid (Table I). The yield of the acrylamide was high, and hence the pyrolysis of N,N-dimethylacetoxypropionamide affords a convenient method of preparing this polymerizable amide.

The dimethylacrylamide fraction obtained on distillation of the pyrolyzates was acidic. Acetic acid, identified as its *p*-bromophenacyl ester, appeared to be the principal acidic impurity. Redistillation of this fraction through efficient columns and distillation in the presence of materials that distil azeotropically with acetic acid did not cause satisfactory fractionation. The acidic impurities (approximately 15% by weight calculated as acetic acid), however, could be removed by shaking with sodium carbonate or sodium hydroxide.

Ruhoff and Reid[16] reported that N,N-dimethylpropionamide and propionic acid form a maximum boiling azeotrope.

In experiment 8 (Table I) a large quantity of the acetoxy amide was pyrolyzed, and the pyrolyzate was examined to determine the by-products. The following were found (moles per mole of acetoxy amide decomposed): water, 0.085; hydrogen, 0.05; carbon monoxide, 0.05; unsaturated hydrocarbon gases, 0.01; and diacetyl, trace (indicated by nickel dimethylglyoxime test). On standing, the high-boiling fraction (consisting primarily of the recovered acetoxy amide) deposited an unidentified water-soluble solid (m. p. 140–144° dec.).

N,N-Dimethylacrylamide was mass and solution (aqueous) polymerized, benzoyl peroxide and

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(14) R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400 (1935); P. D. Ritchie, *ibid.*, 1054 (1935).

(15) C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **67**, 56 (1945).

(16) J. R. Ruhoff and E. E. Reid, *ibid.*, **59**, 401 (1937).

ammonium persulfate, respectively, being used as initiators. The polymer was hard, transparent and soluble in water. It was insoluble in heptane and a 50–50 mixture of heptane and toluene, but softened by ethyl acetate and toluene. Aqueous solutions of the polymer were viscous.

The authors are grateful to William A. Faucette for assistance in preparing the amides, H. Betty Wyman and Ruth W. Brand for most of the analytical data, and Clinton Industries, Inc., Clinton, Iowa, for a sample of optically active lactic acid.

Experimental

N,N-Dimethyllactamide.—A mixture of 156 g. (1.5 moles) of methyl lactate, 67.5 g. (1.5 moles) of dimethylamine, and 5 drops of concentrated sulfuric acid was allowed to stand in a closed bottle at room temperature for three weeks. The sulfuric acid was neutralized with sodium acetate, and the resulting mixture was distilled. The yield of amide [b. p. 56–57° (0.6 mm.); d^{20}_{4} 1.0508; n^{20}_{D} 1.4588] was 86%.

Anal. Calcd. for $C_5H_{11}O_2N$: N, 11.96; $\mathrm{M}^{20}_{\mathrm{D}}$ 30.77. Found: N, 11.77; $\mathrm{M}^{20}_{\mathrm{D}}$ 30.47.

In subsequent preparations in which sulfuric acid was not used, yields of 89 and 83%, respectively, were obtained by allowing the methyl lactate–dimethylamine mixture to stand at room temperature for 3 weeks and at about 30° for twenty-four hours. Previous investigators[17] obtained a 60% yield in six hours at 70°.

N,N-Dimethyl-α-acetoxypropionamide.—This compound was prepared from the lactamide with four acetylating agents.

Acetic Anhydride.—To 280 g. (2.4 moles) of dimethyllactamide was added 10% excess acetic anhydride and 0.3 ml. concentrated sulfuric acid, and the mixture heated on a steam-bath; the temperature (exothermic reaction) went to 140°. The sulfuric acid was neutralized with anhydrous sodium acetate, and the mixture was distilled [97% yield; b. p., 67.5° (0.3 mm.); d^{20}_{4} 1.0681; n^{20}_{D} 1.4530]. The distillate solidified (m. p. 44–46°).

Anal. Calcd. for $C_7H_{13}O_3N$: N, 8.80; saponification equivalent, 159.2; $\mathrm{M}^{20}_{\mathrm{D}}$ 40.13. Found: N, 8.81; saponification equivalent, 159.8, $\mathrm{M}^{20}_{\mathrm{D}}$ 40.21.

When a sample of the amide obtained in a subsequent preparation was observed to melt at 56.5–59°, it was suspected that optical isomerism was responsible. The preparation of the dimethylacetoxypropionamide was repeated several times and the products were carefully examined to throw light on this point. A sample of the higher melting material was recrystallized several times from ether, and dried under vacuum for two hours at 40°. The specific rotation, $[\alpha]^{25}_{\mathrm{D}}$ (2 g. in 50 ml. water, 2-dcm. tube) was −42.5°; the m. p. was 56–61°. This material was somewhat hygroscopic, but after overnight drying in air it melted at 60–61° and was not hygroscopic.

Anal. Calcd. for $C_7H_{13}O_3N$: N, 8.80; C, 52.81; H, 8.23; sapon. equiv., 159.2. Found: N, 8.75; C, 52.68; H, 8.32; sapon. equiv., 159.0, $[\alpha]^{25}_{\mathrm{D}}$ (1.01 g. in 50 ml. H_2O, 2-dcm. tube), −47.80°.

The amide was then made from essentially optically inactive methyl lactate. After repeated recrystallization from ether and drying over phosphorus pentoxide two days under vacuum, the m. p. (measured in vacuum) was 34–35°. This material deliquesced rapidly in air. After redistillation through an efficient column, a sample showed $[\alpha]^{25}_{\mathrm{D}}$ (super-cooled liquid, 2-dcm. tube) −0.3°; *i. e.*, it was substantially inactive.

Anal. Found: N, 8.76; C, 53.36; H, 8.35; sapon. equiv., 159.0.

The dimethylacetoxypropionamide was then made from optically active lactic acid, stated to contain 95% of the acid as the *l*(+)-isomer.[18]

The methyl lactate prepared from the active lactic acid had $[\alpha]^{25}_{\mathrm{D}}$ (2-dcm. tube) of −5.28°. Purdie and Irvine[19] have recorded $[\alpha]^{25}_{\mathrm{D}}$ of −8.25°. The acetoxy amide prepared from this sample of methyl lactate was recrystallized from ether: m. p. 58–61.5°; N found 8.87; $[\alpha]^{25}_{\mathrm{D}}$ (0.14 g. in 10 ml. of water, 2-dcm. capillary tube), −46.1°. The literature[20] reports $[\alpha]_{\mathrm{D}}$ +28° and m. p. 57–58° for the acetoxy amide from *d*(−)-lactic acid, and m. p. 48° for the *dl*-acetoxy amide.

Acetic Acid.—A mixture of 117 g. (1 mole) of dimethyllactamide, 240 g. (4 moles) of acetic acid, 200 ml. of benzene and 0.5 ml. of concentrated sulfuric acid was refluxed for twenty-seven hours, a 10-g. aqueous layer (containing 5 g. of water) was obtained in the Dean and Stark tube. The catalyst was neutralized with sodium acetate. Upon distillation, the mixture yielded 87 g. (0.74 mole) of unreacted hydroxy amide and 19 g. (0.12 mole) (48% yield) of acetoxy amide.

Vinyl Acetate.—To 117 g. (1 mole) of N,N-dimethyllactamide containing 1 g. of potassium cyanide was added slowly (heating and stirring) 86 g. (1 mole) of vinyl acetate.[21] When about one-half the vinyl acetate had been added, the mixture warmed spontaneously and required cooling. At the end of the addition of vinyl acetate the mixture was heated to 65° and allowed to stand overnight. The mixture was distilled, giving 55 g. (0.47 mole) of unreacted amide and 80 g. (0.50 mole) of acetoxy amide (94% yield).

Ketene.—Ketene prepared by pyrolyzing acetone in a ketene lamp was passed through 117 g. (1 mole) of dimethyllactamide at room temperature for approximately twelve hours. Upon distillation, 33 g. (0.28 mole) of unreacted amide and 88 g. (0.55 mole) (76% yield) of acetoxy amide were obtained.

N,N-Dimethylacrylamide from Acrylyl Chloride.—Dimethylamine (53 g., 1.2 moles) was passed into an ice-cold benzene solution containing 54 g. (0.6 mole) of acrylyl chloride.[22] The dimethylacrylamide (68% yield) was obtained by filtration followed by distillation of the filtrate, b. p., 83–83.5° (21 mm.); d^{20}_{4} 0.9653; n^{20}_{D} 1.4738; $\mathrm{M}^{20}_{\mathrm{D}}$ calcd., 28.77; found, 28.84; N, calcd. 14.13; found, 14.23.

Boiling points of dimethylacrylamide at different pressures are given in Fig. 1 (b. p. of N,N-dimethylpropionamide obtained from reference 16).

Pyrolysis Experiments.—A small bellows pump[23] delivered the reagent to the top of the vertical Pyrex glass pyrolysis tube, 3.0 cm. in diameter and heated over 30 cm. by an electric furnace. The tube was packed with short lengths of Pyrex glass tubing, and had an axial thermocouple well extending through the heated zone. A second well was located between the tube and furnace.

Each temperature of Table I is the average of the highest temperature in each well, found by probing after a steady state was reached; the outer and inner maxima were usually not more than 10° apart. Most of the reaction was assumed to take place in the free volume within 15° of the maximum temperature, and the contact times were computed on that basis.

The furnace was controlled automatically by a pyrometer connected to a thermocouple located between the tube and furnace. The temperature of each of the well thermocouples was measured with a portable potentiometer, using a standard calibration chart.

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[17] K. Freudenberg, W. Kuhn and I. Bumann, *Ber.*, **63B**, 2380 (1930).

[18] This acid was converted into methyl lactate by a small scale modification of the method of E. M. Filachione and C. H. Fisher, *Ind. Eng. Chem.*, **38**, 228 (1946).

[19] T. Purdie and J. C. Irvine, *J. Chem. Soc.*, **75**, 484 (1899).

[20] K. Freudenberg and L. Markert, *Ber.*, **60B**, 2447 (1927).

[21] V. L. Hansley (U. S. Patent 2,355,971, Aug. 15, 1944) acetylated methyl lactate with vinyl acetate.

[22] C. E. Rehberg, Marion B. Dixon and C. H. Fisher, THIS JOURNAL, **67**, 208 (1945).

[23] B. B. Corson and W. J. Cerveny, *Ind. Eng. Chem., Anal. Ed.*, **14**, 899 (1942).

Nitrogen was used to flush the system before and after each experiment and a very small stream was fed through the tube during the experiment.

The pyrolyzate issuing from the hot portion was cooled to condense vapors; permanent gases were collected over acid–salt solution. The liquid product was distilled (after a small amount of hydroquinone was added to prevent polymerization) to determine the nature and amounts of the products.

Acrylamide–Acid Fractions.—Even when an efficient column was used to distill the dimethylacetoxypropionamide pyrolyzates, the yield of the acrylamide fraction was high (Table I), and titration of this fraction revealed an acid (approximately 15%, computed as acetic). A very careful redistillation of the acrylamide fraction from the pyrolyzate of experiment 8 through a 50-plate column did not isolate two fractions of the same acid content or refractive index, despite boiling point constancy. The acid contents in this distillation ranged from 70 to 2%; the average content was 21%. In a number of instances a *p*-bromophenacyl ester of the acid was obtained from the sodium salt and *p*-bromophenacyl bromide; it melted at 84–85° and when mixed with authentic *p*-bromophenacyl acetate the melting point of the mixture was the same. On the basis of the melting point of the bromophenacyl ester and the discrepancy between titratable acidity and acetic acid recovered from the pyrolyzates by distillation (Table I), it is believed that most or all of the acid associated with the acrylamide was acetic acid.

Several unsuccessful attempts were made to separate the acid and the acrylamide by azeotropic distillation. Excess heptane was added to one sample of the impure dimethylacrylamide to strip out acetic acid as the heptane–acetic acid azeotrope. The heptane distilled almost acid free. To another sample was added excess toluene for a similar purpose. Here some acid was removed, but a 300% excess of toluene removed less than half the acid. A third sample was distilled with a 500% excess of triethylamine to distil out the high-boiling acid–amine azeotrope,[24] but no appreciable purification resulted.

A synthetic mixture of dimethylacrylamide (prepared from acrylyl chloride and dimethylamine), glacial acetic acid and heptane was not effectively fractionated into pure components by a 37-plate still; the heptane fractions contained 5 to 6% acetic acid and the amide fractions 6 to 39% acid. No pure acid was obtained.

The most satisfactory method of purifying the dimethylacrylamide comprised treating the acidic amide fraction with either excess anhydrous sodium carbonate or the theoretical quantity of 50% aqueous sodium hydroxide, filtering and distilling the filtrate (in the presence of hydroquinone) under reduced pressure. The recovery of dimethylacrylamide (containing about 2% acid) after one such treatment was approximately 70%. Dimethylacrylamide obtained by the complete removal of acidic impurities (by further treatment with base) followed by redistillation had properties (b. p., 73.5–74° at 16.5 mm.; d^{20}_{4} 0.9651; n^{20}_{D}, 1.4732; M^{20}_{D}, 28.81; N found, 14.25; calcd., 14.13) similar to those of the amide prepared from acrylyl chloride and dimethylamine.

Summary

N,N-Dimethyl-α-acetoxypropionamide resembles methyl α-acetoxypropionate in that thermal decomposition yields acetic acid and the corresponding acrylic acid derivative. Pyrolysis affords a convenient method of converting lactic acid, through the acetyl derivative of N,N-dimethyllactamide, into N,N-dimethylacrylamide. The dimethylacrylamide polymerizes readily, yielding a hard, transparent, water-soluble polymer.

[24] H. S. Van Klooster and W. A. Douglas, *J. Phys. Chem.*, **49**, 67 (1945).

PHILADELPHIA 18, PA. RECEIVED JANUARY 9, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Pentachlorophenyl Derivatives. I. The β-Chlorination of Ethylpentachlorobenzene and the Preparation of Pentachlorostyrene

BY SIDNEY D. ROSS, MOUSHY MARKARIAN AND MATTHEW NAZZEWSKI

It is reported in the patent literature[1] that direct chlorination of ethylpentachlorobenzene gives 1-pentachlorophenyl-1-chloroethane having m. p. 52.5° and b. p. 193–203° at 15 mm. and that, furthermore, treatment of this product with heat or alcoholic potassium hydroxide gives pentachlorostyrene, which boils at 311–312° and is not polymerized by heat, acid or sunlight. We have not found it possible to repeat these results and were consequently led to study the peroxide-catalyzed sulfuryl chloride chlorination as well as the direct chlorination of ethylpentachlorobenzene.

We find that when ethylpentachlorobenzene is heated to 200° and illuminated with a 200-watt unfrosted bulb it rapidly takes up chlorine to give, in addition to recovered starting material, three products, none of which have the properties of the reported 1-pentachlorophenyl-1-chloroethane. The major product is a solid, I, analyzing correctly for $C_8H_4Cl_6$ and melting at 89–90°. It can be recovered unchanged after refluxing for forty-eight hours in glacial acetic acid containing an equivalent of potassium acetate. The same product can be obtained in 55% yield by ring chlorination of 1-phenyl-2-chloroethane by the excellent method of Silberrad[2] which employs sulfuryl chloride as the chlorinating agent and aluminum chloride and sulfur monochloride as the catalysts. This would seem to indicate that I is 1-pentachlorophenyl-2-chloroethane, but since there is some danger of rearrangement in the Silberrad reaction we prepared 1-pentachlorophenyl-1-chloroethane, VI, by the unambiguous route indicated below. Pentachlorotoluene, II, was prepared as directed by Silberrad.[2] It was chlorinated to give pentachlorobenzal chloride, III, following the procedure of Lock.[3] In hydrolyzing III to pentachlorobenzaldehyde, IV, we have

[1] Levine and Cass, "Chlorinated Aromatic Hydrocarbons," U. S. Patent 2,193,823, March 19, 1940.

[2] Silberrad, *J. Chem. Soc.*, **127**, 1267 (1925).

[3] Lock, *Ber.*, **66**, 1527 (1933).