area does not change during use. It is noteworthy that this is about the silver concentration at which the catalytic activity levels off. The increase in area at still higher concentrations is probably due to increases in the area of the upper layers of the silver nitrate itself, accompanying its reduction to metallic silver, which has already been shown to occur. If this latter supposition is correct the increase in area might be expected to become nearly constant at the higher concentrations since data presented earlier indicate that only a limited amount of decomposition can occur. The points lying above 15% total silver which represents the largest amount of silver nitrate which can be decomposed under these conditions, do in fact suggest such a leveling off with ΔS_e equal to about 30 sq. m./g.

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Summary

1. The activity of silver nitrate supported on alumina for reaction with acetylene–air mixtures has been studied as a function of silver nitrate concentration, area of support, temperature of activation, and acetylene concentration. Surface areas and X-ray diffraction patterns have been determined.

2. The activity is found to depend upon the ratio of surface area of support to concentration of silver nitrate, and arguments are advanced to show that maximum activity is attained when the support is covered with a multi-layer of silver nitrate.

3. Evidence is presented which leads to the hypothesis that a certain minimum crystal size is required for reactivity.

4. The effect of changes in activation temperature is related to chemical changes in the silver nitrate.

5. Factors causing decreased activity during the reaction are analyzed, and reduction of silver nitrate in the active layer is shown to occur to a limited extent. The change in surface area during use is found to be related to the decline in activity.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

New Synthetic Methods for the Preparation of Lysine[1]

BY DAVID CYR SAYLES[2] WITH ED. F. DEGERING

Many syntheses of lysine have been published,[3] but only the von Braun[4] method and its improvement by Eck and Marvel[5] and Galat[6] seem to have commercial application. More recently, two closely related syntheses of DL-lysine, using dihydropyran as starting material[7,8] have been published by Rogers[7] and Gaudry.[8]

During this research, several methods were investigated. The first involves the splitting of ϵ-caprolactam[9] by hydrochloric acid and neutralization to give 6-aminohexanoic acid.[10] The rest of the process is similar to that developed by Eck and Marvel.[11] The ammonolysis of 2-bromo-6-benzoylaminohexanoic acid, however, is effected by the use of aqueous ammonia and ammonium carbonate in the presence of cuprous chloride, with a decided increase in yield.

Several methods which entail the use of 1-bromo-4-chlorobutane and 1-chloro-4-nitrobutane were investigated. These intermediates are prepared by direct chlorination of 1-bromobutane and 1-nitrobutane, respectively, in yields of 30–40%. Their utilization in the preparation of lysine are indicated by: n-BuBr → $Cl(CH_2)_4Br$ (35%) → $Cl(CH_2)_4CH(CO_2Et)_2$ (65%) → $Cl(CH_2)_4CBr(CO_2Et)_2$ (70%) → $Cl(CH_2)_4CHBrCO_2H$ (50%) → lysine dihydrochloride (55%).

n-$BuNO_2$ → $Cl(CH_2)_4NO_2$ (35%) → $O_2N(CH_2)_4CH(CO_2Et)_2$ (20%) → $O_2N(CH_2)_4C(:NOH)CO_2Et$ (25%) → $H_2N(CH_2)_4CHNH_2CO_2Et$ (9%) → lysine dihydrochloride (5%).

1,4-Dichlorobutane was first converted to 1-chloro-4-phenoxybutane, as indicated by: $Cl(CH_2)_4Cl$ → $PhO(CH_2)_4Cl$ (60%) → $PhO(CH_2)_4CHAcCO_2Et$ (40%) → $PhO(CH_2)_5CO_2H$ (50%) → $PhO(CH_2)_4CHBrCO_2H$ (85%) → $Br(CH_2)_4CHBrCO_2H$ (87%) → lysine dihydrochloride (81%).

(1) This paper was reported at the Washington meeting of the American Chemical Society in September, 1948.

(2) Present address: Lowe Brothers Company, Dayton, Ohio.

(3) C. L. A. Schmidt, Editor, "The Chemistry of the Amino Acids and Proteins," 2nd ed., Charles C. Thomas, Baltimore, Md., 1944.

(4) J. von Braun, *Ber.*, **42**, 839 (1909).

(5) J. C. Eck and C. S. Marvel, "Org. Syntheses," **19**, 18, 20, 61 (1939).

(6) Galat, THIS JOURNAL, **69**, 86 (1947).

(7) Rogers, Emmick, Tyran, Levine and Scott, report given before the Organic Division of the American Chemical Society at St. Louis in September, 1948.

(8) Gaudry, *Can. J. Research*, **26B**, 387 (1948).

(9) Available from E. I. du Pont de Nemours & Company, Wilmington, Delaware.

(10) Eck, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., 1943, p. 28.

(11) Eck and Marvel, *J. Biol. Chem.*, **106**, 387 (1934).

An alternative method is: $PhO(CH_2)_5CO_2H \rightarrow Br(CH_2)_4CO_2H$ (60%) $\rightarrow Br(CH_2)_4CHBrCO_2H$ (85%) $\rightarrow$ lysine dihydrochloride (81%).

Reduction of monoethyl adipate, either catalytically using copper chromite and hydrogen or sodium and alcohol, yields a mixture of 6-hydroxyhexanoic acid and its lactone which can be converted to 6-bromohexanoic acid and finally lysine.

Experimental

Ammonolysis of 6-Benzoylamino-2-bromohexanoic Acid.—Ammonium hydroxide (250 ml., d. 0.98, 3.75 moles), ammonium carbonate (75 g., 0.9 mole), cuprous chloride (1 g., 0.005 mole) and 6-benzoylamino-2-bromohexanoic acid[11] (70 g., 0.22 mole) are placed in a shaking autoclave and heated at 100 to 150° for twelve to fourteen hours. The solution is then boiled for thirty minutes to decompose the ammonium carbonate, cooled, crystallized, filtered by suction, and washed with alcohol (50 ml.) and then with ether (50 ml.). The aqueous filtrate is evaporated to dryness under reduced pressure, the residue washed with two portions of water (50 ml.), then with ethanol (25 ml.), and finally with ether (25 ml.) to give 55 g. of product (m. p. 260–265°, 98–99%).

Lysine Dihydrochloride.—This compound can be prepared according to the method of Eck and Marvel.[11]

1-Bromo-4-chlorobutane.—A mixture of 1-bromobutane (1000 g., 7.4 moles), sulfuryl chloride[12] (1000 g., 7.4 moles), and benzoyl peroxide (20 g., 0.16 mole) is refluxed for ten to twelve hours until the evolution of gases ceases. The reaction product is then separated by distillation under diminished pressure. The final cut (b. p. 100 to 120° at 100 mm.) is fractionated through a 36-inch glass-packed column (b. p. 110–112° at 100 mm., yield 360 g., 35% of theory).

1-Bromo-4-chlorobutane.—1-Bromobutane (1000 g., 7.4 moles) was placed in a dispersion tube,[13] which was equipped with a condenser attached to a dry ice trap and a hydrogen chloride absorber. Chlorine (519 g., 7.3 moles) is bubbled slowly through the solution, which is illuminated by six 150-watt Mazda light bulbs. The unreacted chlorine is recycled. After complete addition of the chlorine, carbon dioxide is passed through the reaction product to displace the hydrogen chloride. The resulting product is fractionated through a 36-inch column (yield 350 g., 35% of theory, b. p. 110–112° at 100 mm.).

Diethyl 4-Chlorobutylmalonate.—Sodium (96 g., 3.0 moles) is dissolved in absolute alcohol (1000 g.) in a three-necked three-liter flask which is fitted with a mercury-seal stirrer, reflux condenser, dropping funnel, and drying tubes. Then, in order, are added diethyl malonate (480 g., 3.0 moles) and 1-bromo-4-chlorobutane (518 g., 3.0 moles). The reaction mixture is refluxed for four to five hours, the alcohol removed by distillation, and water added to the residue to dissolve the sodium bromide. The oil is separated and the aqueous solution is extracted with ether. The combined organic material is washed with water and dried over anhydrous sodium sulfate. The ether is evaporated, and the residue is distilled under diminished pressure through a 36-inch glass-packed column (500 g., 65% conversion, b. p. 145–148° at 10 mm.).

Diethyl 4-Chlorobutylbromomalonate.—A mixture of diethyl 4-chlorobutylmalonate (550 g., 2.2 moles) and chloroform (1000 ml.) is placed in a three-liter three-necked flask which is fitted with a stirrer, dropping funnel, reflux condenser, and drying tubes. Iodine (5 g.) is added, and then bromine (365 g., 2.3 moles) dissolved in chloroform (200 ml.) is added dropwise. The reaction mixture is then refluxed on a steam-bath for two to three hours until the evolution of hydrogen bromide ceases. The chloroform is recovered and the residue distilled under diminished pressure (b. p. 147–155° at 30 mm., yield 340 g., 70% of theory).

(12) Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

(13) Degering, *Ind. Eng. Chem.*, **24**, 181 (1932).

2-Bromo-6-chlorohexanoic Acid.—Diethyl 4-chlorobutylbromomalonate (387 g., 1.2 moles) is refluxed with concentrated hydrochloric acid (1500 ml., 9.8 moles) containing zinc chloride (100 g., 0.5 mole) for eighteen to twenty-four hours. The reaction mixture is cooled, extracted with benzene, and the benzene extract filtered. The filtrate is then extracted with aqueous sodium carbonate, and the alkaline solution is cooled and acidified with concentrated hydrochloric acid. The organic layer is taken up in ether, and the aqueous solution is then extracted with ether. The combined organic material is washed with water, dried over anhydrous sodium sulfate, and the ethereal solution is filtered, the ether recovered, and the residue distilled under reduced pressure (b. p. 93–95° at 5 mm., yield 135 g., 50% of theory).

Lysine Dihydrochloride.—Ammonium hydroxide (250 ml., 3.75 moles), ammonium carbonate (75 g., 0.87 mole), cuprous chloride (1 g.) and 2-bromo-6-chlorohexanoic acid (57 g., 0.25 mole) are placed in a shaking autoclave and heated at 175–200° for twelve hours. The contents of the autoclave are removed and filtered, the filtrate evaporated to dryness under diminished pressure, and concentrated hydrochloric acid (1000 ml., 6.6 moles) is added to the residue, which is then warmed for ten to fifteen minutes on a steam-bath. The solution is then evaporated, hot absolute alcohol (200 ml.) is added, the solution is filtered, then cooled to 10–15°. A small quantity of absolute ether is added to the filtrate to precipitate any ammonium bromide which is dissolved in the alcohol, and then filtered. Anhydrous ether (200 ml.) is slowly added with continuous stirring to the filtrate. The solid which separates is collected by filtration and dried (m. p. 183–185°, yield 30 g., 55% of theory).

1-Chloro-4-nitrobutane.—1-Nitrobutane (870 g., 7.7 moles) is placed in a dispersion tube[13] equipped with a reflux condenser, which is connected to a Dry Ice trap for the recovery of unreacted chlorine. Phosphorus pentoxide (30 g., 0.1 mole) is added, and chlorine (628 g., 8.9 moles) is slowly bubbled through the solution which is illuminated with nine 150-watt Mazda bulbs. Reaction occurs slowly, with a brief induction period, and the chlorination temperature ranges from 70–80°. The hydrogen chloride is then displaced by a stream of carbon dioxide. The product is poured into water, washed several times with water, and dried over anhydrous sodium sulfate. The material is distilled under reduced pressure (b. p. 100–105° at 10 mm. 370 g., 35% of theory).

Ethyl 2-Acetyl-6-nitrohexanoate.—Sodium (48.3 g., 2.1 moles) is dissolved in absolute alcohol (400 ml.) in a two-liter three-necked flask which is fitted with a mercury-seal stirrer, reflux condenser, dropping funnel, and drying tubes. Ethyl acetoacetate (273 g., 2.1 moles) is added, followed by the slow addition of 1-chloro-4-nitrobutane (214 g., 1.6 moles). The reaction mixture is refluxed on a steam-bath for four to six hours. The alcohol is then distilled, the residue diluted with water, the organic material separated, and the aqueous solution extracted with ether. The combined organic material is washed with water and dried over anhydrous sodium sulfate. The ether is evaporated, and the residue is distilled under diminished pressure (b. p. 153–158° at 9 mm., yield 67 g., 20% conversion).

Ethyl 6-Nitro-2-oximidohexanoate.—Ethyl 2-acetyl-6-nitrohexanoate (160 g., 0.7 mole), chilled to 0°, is mixed with *n*-butyl nitrite (120 g., 1.2 moles), chilled to 0°, and the mixture is then added gradually to a solution of sodium (20 g., 0.95 mole) in cold absolute alcohol (400 ml.) in a one-liter, three-necked flask, which is fitted with a mercury-seal stirrer, dropping funnel, reflux condenser, and drying tubes. The reactants are maintained at −10° for twenty-four to thirty hours by the use of an ice-salt-bath, then permitted to warm up to room temperature, and stirred an additional two to three hours. The alcohol is recovered under diminished pressure, the residue diluted with water, and the organic layer separated. The aqueous solution is extracted with ether, and then the aqueous solution is cooled and acidified with dilute sulfuric acid. The organic layer is again separated, and the aqueous

solution is extracted with ether. The combined organic material is washed with water, and then dried over anhydrous sodium sulfate (yield 38 g., 25% conversion).

Lysine Dihydrochloride.—Tin (60 g., 0.5 mole), water (60 ml.) and ethyl 6-nitro-2-oximidohexanoate (10 g., 0.046 mole) are placed in a 500-ml. three-necked flask, which is equipped with a stirrer, dropping funnel, and reflux condenser. Hydrochloric acid (100 ml., 0.65 mole) diluted with water (150 ml.) is slowly added, and the reaction mixture is then refluxed for four to six hours. The excess tin is removed by filtration, the aqueous solution is extracted once with ether, the filtrate is evaporated to dryness, and the residue is dried in a vacuum desiccator over concentrated sulfuric acid. The residue is then transferred to a Soxhlet thimble and extracted with absolute alcohol. The solvent is evaporated, and the residue is refluxed with 50% aqueous alcohol (100 ml.) containing sodium hydroxide (10 g., 0.25 mole) for four to five hours. The alcohol is recovered, the residue is acidified with hydrochloric acid and the solvent is then evaporated under diminished pressure. The residue is dissolved in a small quantity of alcohol, picric acid in alcohol is added, and the monopicrate is isolated. The product darkens above 215° and decomposes at about 233° (yield 0.9 g., 7% of theory).

4-Phenoxybutyl Chloride.—A mixture of water (1000 g.), 1,4-dichlorobutane (320 g., 2.5 moles), and phenol (185 g., 2.0 moles) is placed in a three-liter, three-necked flask which is equipped with a mercury-seal stirrer, reflux condenser, and a dropping funnel. The mixture is heated to boiling, a solution of sodium hydroxide (75 g., 1.9 moles) in water (250 ml.) is slowly added during one to two hours, and the reaction mixture is refluxed for seven to nine hours. The lower layer is separated, washed twice with 10% aqueous sodium hydroxide to remove any unreacted phenol, then washed with water, and finally dried over anhydrous sodium sulfate. The product is then distilled under diminished pressure (b. p. 135–138° at 12 mm., yield 200 g., 60% conversion).

Ethyl 4-Phenoxybutylacetoacetate.—Absolute ethanol (500 ml.) is placed in a two-liter three-necked flask, which is fitted with a mercury-seal stirrer, reflux condenser, dropping funnel, and drying tubes. Sodium (58 g., 2.5 moles) is added. After complete reaction, freshly distilled ethyl acetoacetate (325 g., 2.5 moles) is added dropwise while the reaction mixture is maintained under gentle reflux, and the mixture is then refluxed ten to twelve hours. The solvent is distilled, the residue is diluted with water, the organic material is separated, and the aqueous solution is extracted with ether. The combined organic material is washed with water, dried over anhydrous sodium sulfate, the ether recovered, and the residue distilled under diminished pressure. The distillate consists of unreacted materials, whereas the residue is crude ethyl 4-phenoxybutylacetoacetate, which is an oily, low melting solid (yield 240 g., 40% conversion).

6-Phenoxyhexanoic Acid.—Ethyl 4-phenoxybutylacetoacetate (110 g., 0.4 mole) is heated on a steam-bath for seven to nine hours with a mixture of potassium hydroxide (110 g., 2.0 moles), water (80 ml.) and ethanol (100 ml.)., while vigorously stirring throughout. The mixture is allowed to cool, diluted with water, extracted with ether to remove the alkali-insoluble material, and the alkaline solution boiled with Norite (1 g.) for one-half hour. The solution is filtered, the filtrate cooled in an ice-bath, then acidified with dilute hydrochloric acid, and the solid which separates is filtered, washed with water, and dried in a vacuum desiccator (m. p. 69°, yield 40 g., 50% of theory).

2-Bromo-6-phenoxyhexanoic Acid.—6-Phenoxyhexanoic acid (100 g., 0.5 mole) is placed in a one-liter three-necked flask, which is equipped with an efficient stirrer, reflux condenser, dropping funnel, and drying tubes. Red phosphorus (15 g.) is then added, followed by the cautious addition of a slight excess of bromine (93.5 g., 0.55 mole). The reaction mixture is then heated on a steam-bath for five to six hours, allowed to stand overnight, the product poured into water, and the mixture heated on a steam-bath to ensure the complete hydrolysis of the acid bromide. The acid is dissolved in aqueous sodium carbonate, acidified with dilute aqueous hydrochloric acid, and the acid which separates is filtered, dried in a vacuum desiccator, and crystallized from hexane (m. p. 114–7°, yield 117 g., 85% of theory).

2,6-Dibromohexanoic Acid.—A mixture of 2-bromo-6-phenoxyhexanoic acid (20 g., 0.07 mole) and aqueous hydrobromic acid (200 ml., 48%, 1.7 moles) is refluxed for eight to ten hours. The phenol is steam distilled, the residue is allowed to cool, the acid separated by extraction with ether, and the ethereal solution extracted with dilute aqueous sodium carbonate. The aqueous extract is extracted with ether, and the alkaline solution is acidified with dilute hydrochloric acid. The oil which separates is extracted with ether, the ethereal extract washed with water, dried over anhydrous sodium sulfate, the ether evaporated, and the residue is distilled under diminished pressure (b. p. 144–146° at 2 mm., yield 17.4 g., 87% of theory).

Lysine Dihydrochloride.—A mixture of ammonium hydroxide (110 ml., 1.7 moles), ammonium carbonate (48 g., 0.5 mole), 2,6-dibromohexanoic acid (27.4 g., 0.1 mole) and cuprous chloride (1 g.) is placed in a hydrogenation bomb and heated at 125–150° for eighteen to twenty-four hours. The solution is then removed from the bomb, boiled for ten to twenty minutes to decompose the ammonium carbonate, and then evaporated to dryness under diminished pressure. The residue is treated with hydrochloric acid, evaporated to a thick sirup, dissolved in hot alcohol, and filtered. The filtrate is cooled to 15 to 20°, and absolute ether is slowly added. The solid which separates is collected by filtration, and dried (m. p. 185–189°, yield 18 g., 81% of theory).

6-Bromohexanoic Acid.—This compound can be prepared by the method of Marvel[14] in yields of 60 to 65%, or according to the method of Brown and Partridge[15] in 80% yields, or by the reaction of aqueous hydrogen bromide on 6-hydroxyhexanoic acid and its lactone which is prepared by the reduction of monoethyl adipate.

6-Hydroxyhexanoic Acid.—Monoethyl adipate (180 g., 1.0 mole) is neutralized with potassium hydroxide (30% aqueous), the solution is evaporated to dryness under diminished pressure and then dried in a vacuum desiccator over concentrated sulfuric acid and finally over phosphoric anhydride. Potassium ethyl adipate (106 g., 1.0 mole) is placed in a three-liter, three-necked flask, which is fitted with a reflux condenser, mercury-seal stirrer, and drying tubes. Absolute ethanol (1500 ml.) is added, the solution refluxed to effect as complete solution as possible, and sodium (80 g., 3.5 moles) is then added in small quantities. After the complete disappearance of the sodium metal, the alcohol is removed by distillation, leaving a crude residue of 6-hydroxyhexanoic acid and its lactone in almost quantitative yields.

6-Hydroxyhexanoic Acid.—Monoethyl adipate (200 g., 0.85 mole) and copper chromite catalyst (20 g.) are placed in a hydrogenation bomb. Hydrogen at a pressure of 2000 pounds per square inch is introduced, and the temperature is rapidly raised to 225–250°. Hydrogen is then introduced at intervals so that the hydrogen pressure is maintained above 2000 pounds pressure. The bomb and contents are then allowed to cool to room temperature, the contents removed, the catalyst removed by filtration, and the solvent recovered, yielding a crude residue of 6-hydroxyhexanoic acid and its lactone in almost quantitative yields.

The crude 6-hydroxyhexanoic acid and its lactone are converted directly into 6-bromohexanoic acid.[15]

Summary

Several methods for the synthesis of lysine dihydrochloride have been developed during the course of this research.

The most promising method in this study for the

(14) Marvel, THIS JOURNAL, **46**, 2841 (1924).

(15) Brown and Partridge, *ibid.*, **66**, 839 (1944).

commercial production of this essential amino acid appears to involve the use of ϵ-caprolactam.

The second most practical method involves the reduction of monoethyl adipate, and conversion to 6-bromohexanoic acid.

The conversion of tetramethylene chlorobromide, tetramethylene chloride, 1-nitro-4-chlorobutane to lysine may be somewhat inferior methods but are significant in case raw material values change and the by-products formed in the reactions can be utilized.

LAFAYETTE, INDIANA RECEIVED JANUARY 17, 1949

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Acrylic Esters of Amino Alcohols

BY C. E. REHBERG AND W. A. FAUCETTE[2]

According to the patent literature, several amino alcohols have been converted into the acrylic[3] or methacrylic[4] esters. Gilman and co-workers[5] prepared diethylaminoethyl acrylate hydrochloride, but, since their interest was in its physiological activity, they did not prepare the free ester or make any attempt to polymerize the salt.

Our principal object in preparing the aminoalkyl acrylates was to copolymerize them with alkyl acrylates and thus obtain acrylic elastomers containing basic functional groups. However, they did not readily polymerize alone, nor did they copolymerize with ethyl acrylate. Hence, their properties were not extensively studied.

It has been stated that aminoalkyl methacrylates act as polymerization inhibitors and are difficult to polymerize with benzoyl peroxide[4b] but are readily polymerized by ultraviolet light.[4b] Diethylaminoethyl methacrylate has been reported[4b,d,e] to polymerize spontaneously at 0° in the absence of light or catalysts. In general, these observations were confirmed in the present work with acrylic esters.

Experimental

Amino Alcohols.—The diethyl- and dibutylaminopropanols were obtained from Eastman Kodak Company; dimethylaminoethanol and 2-N-morpholinoethanol were kindly supplied by the Carbide and Carbon Chemicals Corporation, and we are indebted to Sharples Chemicals, Inc., for diethyl- and dibutylaminoethanol and ethyldiethanolamine. All were used after a simple distillation.

TABLE I

PREPARATION AND PROPERTIES OF AMINOALKYL ACRYLATES

Acrylate	Boiling point °C.	Mm.	Yield, %	$n^{20}D$	d^{20}_4	Mol. refraction Calcd.	Found	Nitrogen Calcd.	Found
Dimethylaminoethyl	61	11	36	1.4375	0.9434	39.65	39.80	9.8	9.2
Diethylaminoethyl	70	5	94	1.4425	.9251	48.89	49.02	8.2	8.3
2-(1,1′-Dibutylamino)-ethyl	82	0.3	93	1.4460	.8977	67.36	67.53	6.2	6.4
3-Diethylaminopropyl	44	.1	65	1.4441	.9180	53.50	53.61	7.6	7.5
2-(1,1′-Dibutylamino)-propyl	77	.2	40	1.4440	.8880	71.98	72.20	5.8	5.4
3-(1,1′-Dibutylamino)-propyl	83	.2	85	1.4480	.8952	71.98	72.18	5.8	5.6
2-N-Morpholinoethyl	67	.2	96	1.4728	1.0711	48.33	48.49	7.6	7.6
N-Ethyl-N-(2-hydroxyethyl)-aminoethyl	77	.2	76	1.4662	1.0211	50.41	50.79	7.4	8.3

The aminoalkyl acrylates (Table I) were prepared readily, and usually in high yield, by the alcoholysis of methyl or ethyl acrylate. This method had been used previously in the preparation of alkyl,[6] alkenyl[7] and alkoxyalkyl[8] acrylates.

Monomeric Acrylates.—The esters were prepared by the alcoholysis of methyl or ethyl acrylate. Aluminum isopropoxide was used as a catalyst and phenyl-β-naphthylamine as a polymerization inhibitor. In one experiment, no inhibitor was used, and a lowered yield of monomer, together with a large distillation residue, was obtained. The procedure and equipment have been described in previous papers.[6-8]

In the one experiment in which ethyldiethanolamine was used, only one mole of methanol was produced in the reaction. The molecular refraction of the constant-boiling product agreed with the expected value for the monoacrylate. The nitrogen analysis was somewhat high for the monoacrylate, indicating that some free amine was present. However, two fractional distillations through a 3-ft. Vigreux column failed to effect any separation.

The esters were colorless liquids having mild, ammoniacal odors and appreciable water solubility.

Polymerization Experiments.—Addition of benzoyl peroxide (1%) to the monomers or to their solutions (10%) in ethyl acetate resulted in instant discoloration. Sub-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Present address: Corn Products Refining Company, Argo, Illinois.

(3) Graves, U. S. Patent 2,138,031, November 29, 1938.

(4) (a) Heckert, *ibid.*, 2,168,338, August 8, 1939; (b) Graves, *ibid.*, 2,138,763, November 29, 1938; (c) Harmon, *ibid.*, 2,138,762, November 29, 1938; (d) Izard, *ibid.*, 2,129,694, September 13, 1938; (e) Barrett and Strain, *ibid.*, 2,129,662, September 13, 1938.

(5) Gilman, Heckert and McCracken, THIS JOURNAL, **50**, 437 (1928).

(6) (a) Rehberg and Fisher, THIS JOURNAL, **66**, 1203 (1944); (b) Rehberg, Faucette and Fisher, *ibid.*, 1723; (c) Rehberg, *Org. Syntheses*, **26**, 18 (1946).

(7) Rehberg and Fisher, *J. Org. Chem.*, **12**, 226 (1947).

(8) Rehberg and Faucette, "Acrylic Esters of Ether-Alcohols," submitted for publication in *J. Org. Chem.*