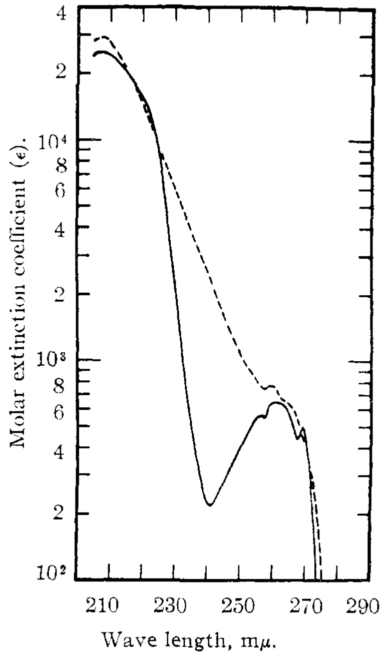

Fig. 2.—Ultraviolet absorption spectra of $Ph_2CHCH_2Ph$ (———) and triphenylsuccinic anhydride (VIII) (--------) in 95% ethyl alcohol.

except that at the end of the one hour reaction period 50 ml. of *t*-amyl alcohol was added cautiously to the refluxing reaction mixture and stirring continued for 15 minutes. Finally 50 ml. of 95% ethyl alcohol was added to decompose a little remaining sodium. Neutralization with hydrochloric acid, concentration, and extraction with ether gave 17.3 g. of light brown product of m.p. 53.8–56.0°. Decolorization with Nuchar C and crystallization from ethyl alcohol gave 14.0 g. of white crystals of m.p. 55.0–56.2° as expected for 1,1,2-triphenylethane.[15,29] Two sublimations *in vacuo* at 0.07 mm. gave crystals of m.p. 55.5–56.7° which were used as standard for 1,1,2-triphenylethane in the infrared analyses.

**Absorption Spectra.**—Ultraviolet absorption spectra were determined by means of a Beckman quartz spectrophotometer, model DU. Quantitative analyses for 1-chloro-1,2,2-triphenylethene (I) were made at 290 or 300 mμ and probably were accurate within 5% composition by weight. It was assumed that all of the absorption at this wave length was due to I since triphenylethylene, which has a similar absorption band, reacts much more rapidly with phosphorus pentachloride than does 1,1,1-triphenylethane or 2-chloro-1,1,1-triphenylethane (II).

Infrared spectra were determined with a Perkin–Elmer double beam model 21 infrared spectrophotometer. Quantitative analyses for mixtures of 1,1,1-triphenylethane were made in 0.5-mm. rock salt cells upon solutions containing 0.450 g. of triphenylethane in 5.00 ml. of carbon disulfide. Analyses were conducted at wave lengths of 8.238, 9.359, 9.449 and 12.719 μ which correspond to maxima of 1,1,1-triphenylethane at the first and third wave lengths and of 1,1,2-triphenylethane at the remaining wave lengths. Analyses at 9.449 μ were made only for samples which were predominantly 1,1,1-triphenylethane because of the rather steep slope of the absorption curve of 1,1,2-triphenylethane in this region. Compositions were read from nearly linear empirical calibration curves prepared from synthetic mixtures of the triphenylethanes. Analyses are reported as the average of the three or four values so obtained along with the mean deviation from the average.

**Acknowledgment.**—The author wishes to acknowledge partial support of this research by a Frederick Gardner Cottrell Grant from the Research Corporation of New York.

(29) A. Klages and S. Heilmann, *Ber.*, **37**, 1455 (1904).

Atlanta, Ga.

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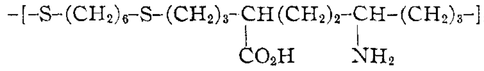
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

# The Synthesis of a Polyampholyte of Regular Structure[1,2]

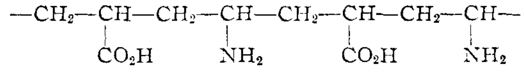
By C. S. Marvel and Wendell W. Moyer, Jr.

Received May 6, 1957

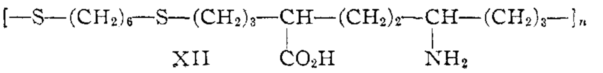
A polyampholyte of the structure

$-[-S-(CH_2)_6-S-(CH_2)_3-\underset{CO_2H}{CH}(CH_2)_2-\underset{NH_2}{CH}-(CH_2)_3-]_n-$ has been synthesized.

With but one exception all previously reported synthetic polyampholytes have been obtained by copolymerization techniques using acidic and basic monomers such as vinylpyridine and acrylic acid, or 2-dimethylaminoethyl methacrylate and vinylsulfonic acid. The composition of these copolymers may be determined, but the composition gives no real indication of the internal structure of the copolymer.

The only known synthetic polyampholyte not prepared by copolymerization techniques is the one reported by Vrancken and Smets.[3] They described the synthesis of a fairly regular polyampholyte from polyacrylyl chloride by the Curtius and Lossen type rearrangement) whose acidic and basic functions largely alternate along the backbone of the polymer as


$$-CH_2-\underset{CO_2H}{CH}-CH_2-\underset{NH_2}{CH}-CH_2-\underset{CO_2H}{CH}-CH_2-\underset{NH_2}{CH}-$$

While this polyampholyte undoubtedly has for the most part a regular alternation of the acidic and basic functions, the amphoteric units are close together and thus the electrical interactions are greatly complicated. This paper describes the synthesis of a polyampholyte having unequivocally regular, isolated amphoteric units.


$$[-S-(CH_2)_6-S-(CH_2)_3-\underset{CO_2H}{CH}-(CH_2)_2-\underset{NH_2}{CH}-(CH_2)_3-]_n$$

XII

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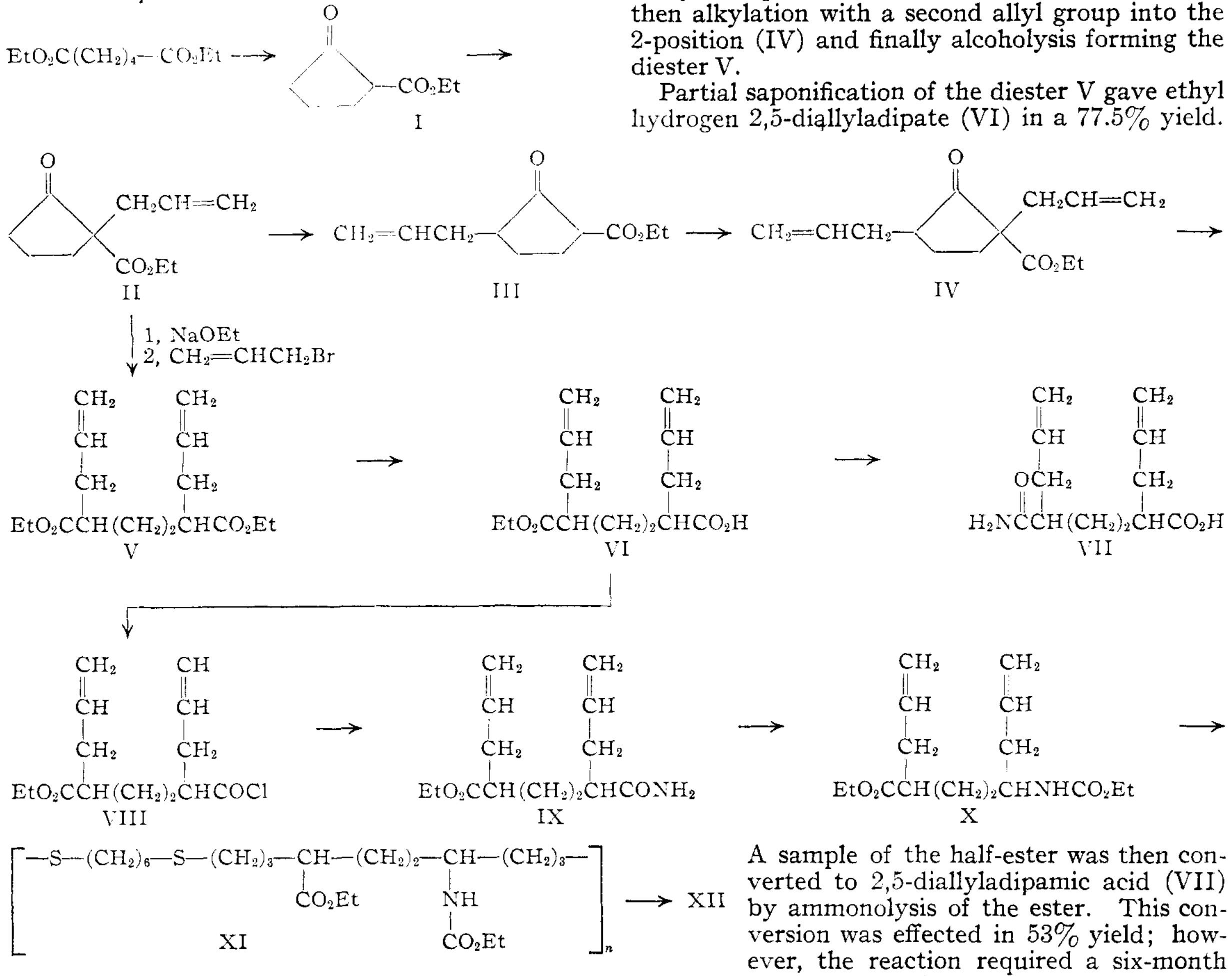
[1] The work discussed herein was performed as a part of the polymer research project sponsored by the National Science Foundation.

[2] Abstracted from a portion of a thesis submitted in partial fulfillment of requirements for the Ph.D. degree by Wendell William Moyer, Jr., to the Graduate College of the University of Illinois in 1957.

[3] M. Vrancken and G. Smets, *J. Polymer Sci.*, **14**, 521 (1954).

The synthesis was accomplished by the following series of steps.



Ethyl cyclopentanone-2-carboxylate (I) was prepared from diethyl adipate by a Dieckmann condensation in 88% yield. The 2-allyl derivative II was then made in 90% yield by a general alkylation procedure. Isomerization of the 2-allyl compound II to the 5-allyl derivative III was effected by the general method originally discovered by Openshaw and Robinson[4] for isomerization of a cyclohexanone derivative and applied by Chatterjee and her coworkers[5,6] to cyclopentanone derivatives. The yield of ethyl cyclopentanone-5-allyl-2-carboxylate (III) was 78%. A second allyl group was then introduced into the 2-position giving ethyl cyclopentanone-2,5-diallyl-2-carboxylate (IV) in 72% yield. Treatment of IV with sodium ethoxide gave diethyl 2,5-diallyladipate (V).

In the course of repeating the synthesis of ethyl cyclopentanone-2,5-diallyl adipate (IV), it was found that treatment of ethyl cyclopentanone-2-allyl-2-carboxylate (II) first with sodium ethoxide under the conditions which previously had led to isolation of the 5-allyl derivative III, and then with allyl bromide gave diethyl 2,5-diallyladipate (V) in an over-all yield of 93.5%. The course of this reaction no doubt involves first isomerization of the 2-allyl compound II to the 5-allyl derivative III, then alkylation with a second allyl group into the 2-position (IV) and finally alcoholysis forming the diester V.

Partial saponification of the diester V gave ethyl hydrogen 2,5-diallyladipate (VI) in a 77.5% yield.

A sample of the half-ester was then converted to 2,5-diallyladipamic acid (VII) by ammonolysis of the ester. This conversion was effected in 53% yield; however, the reaction required a six-month reaction time and was eliminated as a useful synthetic procedure because of this fact. Conversion of the half-ester to ethyl 2,5-diallyladipoylate chloride (VIII) was accomplished in a 95% yield of the crude material. Ammonolysis of the acid chloride VIII gave ethyl 2,5-diallyladipamate (IX). The yield of the crude ester-amide IX was 88%.

A Hofmann hypobromite rearrangement of the ester-amide IX using bromine and sodium ethoxide gave a 42% yield of monomer X.

The monomer X was copolymerized with hexamethylenedithiol by the general emulsion polymerization technique developed in this Laboratory for the co-polymerization of diolefins with dimercaptans.[7] The polymer XI was obtained in consistently high percentage conversions, usually 90–100%; however, only relatively low molecular weight polymer was produced (inherent viscosity 0.09 to 0.13). Precoagulation of the polymers during the emulsion polymerization occurred in all experiments, and it is believed that the failure to obtain high molecular weight polymers was due primarily to this factor.

Complete hydrolysis of the polymer XI to the

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(4) H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 941 (1937).

(5) N. N. Chatterjee, B. K. Das and G. N. Barpujari, *J. Indian Chem. Soc.*, **17**, 161 (1940).

(6) N. N. Chatterjee and A. Bose, *Science and Culture*, **6**, 724 (1941).

(7) For the thirteenth communication on this topic, see C. S. Marvel and L. E. Olson, *J. Polymer Sci.*, **17**, in press (1957).

polyampholyte XII was accomplished only with difficulty. Treatment of the polymer XI with aqueous alkali in a platinum dish in an autoclave heated to 125° and 24 p.s.i. for periods of at least one week gave satisfactory results. Careful neutralization of the alkaline reaction mixture followed by dialysis, and finally lyophilization to complete dryness gave the pure polyampholyte XII in the form of a white, fluffy powder.

The properties of this polymer are being investigated by Professor F. T. Wall of this Laboratory.

## Experimental

**Ethyl Cyclopentanone-2-carboxylate (I).**—This compound was prepared according to the directions given in reference 8. A yield of 205.5 g. (87.6%) was obtained; b.p. 105.5–107.5° (16 mm.), $n^{25}_{\mathrm{D}}$ 1.4507.

The semicarbazone derivative was made according to the general method of Shriner and Turner.[9] The product was obtained in good yield and was recrystallized once from 25% ethanol; m.p. 142.5° (reported[10] 143°).

**Ethyl Cyclopentanone-2-allyl-2-carboxylate (II).**—The general method of Rudolf Grewe[11] for the preparation of ethyl cyclohexanone-2-allyl-2-carboxylate was used in the preparation of the corresponding cyclopentanone compound. To a suspension of 28.3 g. (1.23 g. atoms) of powdered sodium in 1200 ml. of dry xylene was added 195.0 g. (1.25 moles) of ethyl cyclopentanone-2-carboxylate (I) slowly with stirring over a period of one-half hour. After this addition was complete, the reaction mixture was heated gently under reflux with stirring for one hour. Redistilled allyl bromide, 158.0 g. (1.30 moles), was then added dropwise to the hot reaction mixture and the resulting mixture was heated under reflux with stirring for five hours. The flask was allowed to cool to room temperature and then was immersed in an ice-bath. After allowing sufficient time for the contents of the flask to cool to the ice-bath temperature, 1 l. of ice-cold water was added. The xylene layer was separated from the aqueous layer in a separatory funnel and was extracted once with 500 ml. of water. The combined aqueous extracts were extracted once with 300 ml. of benzene, the benzene extract being added to the xylene layer. The combined benzene–xylene solution was transferred to a distillation flask and the solvents removed by distillation at reduced pressure. The crude product was distilled under diminished pressure through a 12-inch column packed with Berl saddles yielding 221 g. (90.2%), b.p. 83–86° (2.25 mm.) (reported[12] b.p. 119° at 8 mm.), $n^{18.2}_{\mathrm{D}}$ 1.4648).

*Anal.*[13] Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.58; H, 8.09.

The infrared spectrum[14] contains bands assignable to an aliphatic ester function (1752, 1231 cm.$^{-1}$), to a ketone 1727 cm.$^{-1}$), and to a terminal vinyl group (1647, 1009 and 926 cm.$^{-1}$).

The semicarbazone derivative was prepared and recrystallized twice from 25% ethanol, yielding an analytically pure sample, m.p. 146–146.5°. The infrared spectrum was in agreement with the expected structure.

*Anal.* Calcd. for $C_{12}H_{19}N_3O_3$: C, 56.90; H, 7.56; N, 16.59. Found: C, 57.13; H, 7.43; N, 16.36.

**Ethyl Cyclopentanone-5-allyl-2-carboxylate (III).**—The general method of Chatterjee, Das and Barpujari[5] for the rearrangement of diethyl cyclopentanone-2-carboxylate-2-acetate to the diethyl 5-carboxylate-2-acetate derivative was used. An alcoholic sodium ethoxide solution of 6.0 g. (0.26 g. atom) of sodium in 65 ml. of absolute ethanol and 49.0 g. (0.25 mole) of ethyl cyclopentanone-2-allyl-2-carboxylate (II) was heated with stirring under gentle reflux for eight hours. After cooling the flask in an ice-bath, the solution was treated with ice-cold dilute sulfuric acid until it gave a distinctly acid reaction to congo red paper. The solution was then extracted with ether several times; the combined ethereal extracts washed once with 5% sodium bicarbonate solution and once with water, and then dried overnight over sodium sulfate. After transferring the ether solution to a distilling flask, the ether was removed by distillation at ordinary pressure and the residual liquid was fractionated at reduced pressure. The product was obtained in a yield of 38.0 g. (77.6%), b.p. 92–95° (2.25 mm.), $n^{22.5}_{\mathrm{D}}$ 1.4638. The infrared spectrum contains bands assignable to an aliphatic ester (1752, 1196 cm.$^{-1}$), to an enolizable keto-ester (1725, 1624 and 1661 cm.$^{-1}$), and to a terminal vinyl group (1643, 1015 and 918 cm.$^{-1}$).

*Anal.* Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.31; H, 8.25.

The semicarbazone was prepared and purified by trituration with boiling water; m.p. 125.5–126°. The infrared spectrum was in agreement with the expected structure.

*Anal.* Calcd. for $C_{12}H_{19}N_3O_3$: C, 56.90; H, 7.56. Found: C, 56.99; H, 7.60.

**Ethyl Cyclopentanone-2,5-diallyl-2-carboxylate (IV).**—The general alkylation method of Grewe[11] was utilized. To a warmed reaction mixture of 3.68 g. (0.16 g. atom) of powdered sodium in 200 ml. of dry xylene was added 32.7 g. (0.167 mole) of ethyl cyclopentanone-5-allyl-2-carboxylate. After the addition was complete, the mixture was heated under reflux with stirring for three hours. Allyl bromide, 20.57 g. (0.17 mole), was added in a dropwise manner and the reaction mixture was heated under reflux with stirring for five hours. The reaction flask was then cooled to room temperature and immersed in an ice-bath. Ice chips were carefully introduced followed by 150 ml. of water. The aqueous layer was separated from the xylene solution and was extracted once with 50 ml. of benzene. The benzene extract was added to the xylene and the combined solution was washed once with 100 ml. of water. The combined benzene–xylene solution was transferred to a distilling flask and the solvents were removed by distillation at reduced pressure. Distillation of the residual liquid under diminished pressure through a 12-inch column packed with Berl saddles yielded 28.7 g. of product (72%), b.p. 104–106° (2.25 mm.), $n^{22.5}_{\mathrm{D}}$ 1.4692. The infrared spectrum contains bands assignable to an aliphatic ester (1745, 1222 cm.$^{-1}$), to a ketone (1724 cm.$^{-1}$), and to a terminal vinyl group (1643, 999 and 918 cm.$^{-1}$).

*Anal.* Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.11; H, 8.76.

**Diethyl 2,5-Diallyladipate (V) from Ethyl Cyclopentanone-2,5-diallyl-2-carboxylate (IV).**—A solution prepared from 0.1 g. of sodium and 50 ml. of absolute ethanol and 4.1 g. of ethyl cyclopentanone-2,5-diallyl-2-carboxylate (IV) was heated under reflux for three hours. After cooling, the reaction mixture was poured with stirring into 300 ml. of ice-cold acidified (hydrochloric acid) water and the aqueous mixture was then extracted with four 50-ml. portions of ether. Evaporation of the ether followed by a fractional distillation of the remaining liquid at reduced pressure through a 10-inch Vigreux column yielded 1.2 g., b.p. 113–114° (1.4 mm.), $n^{20}_{\mathrm{D}}$ 1.4532. The infrared spectrum contains bands assignable to an aliphatic ester (1737, 1187 and 1165 cm.$^{-1}$) and to a terminal vinyl group (1648, 1000 and 922 cm.$^{-1}$).

**Diethyl 2,5-Diallyladipate (V) from Ethyl Cyclopentanone-2-allyl-2-carboxylate (II).**—An alcoholic sodium ethoxide solution of 23.9 g. (1.04 g. atoms) of sodium in 260 ml. of absolute ethanol and 196.3 g. (1.0 mole) of ethyl cyclopentanone-2-allyl-2-carboxylate (II) was heated under gentle reflux with stirring for eight hours. To the hot solution was then added 133.1 g. (1.1 moles) of allyl bromide in a dropwise manner, followed by an additional 50 ml. of absolute ethanol. The solution was heated under reflux with stirring for eight additional hours during which time sodium bromide precipitated. After cooling, the reaction mixture was poured into 1 l. of acidified (hydrochloric acid) water. The aqueous layer was separated and extracted once with 200 ml. of benzene. The benzene extract was added to the organic layer. The organic layer was then extracted once with 100 ml. of 5% sodium bicarbonate solution and once

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[8] P. S. Pinkney, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 119.

[9] R. L. Shriner and T. A. Turner, THIS JOURNAL, **52**, 1267 (1930).

[10] M. L. Bouveault, *Bull. soc. chim.*, [3] **21**, 1019 (1899).

[11] R. Grewe, *Ber.*, **76B**, 1072 (1943).

[12] G. Varon and A. Horeau, *Bull. soc. chim.*, [5] **1**, 1703 (1934).

[13] Microanalyses were performed by Mr. Jozsef Nemeth, Mrs. Ruby Ju, Mrs. Maria Stingl, Miss Claire Higham; Clark Microanalytical Laboratories, Urbana, Ill.; and Micro-Tech Laboratories, Skokie, Ill.

[14] The infrared spectra were determined by Mr. James Brader and Mrs. M. Louise Griffing.

with 200 ml. of water. The solvent, benzene, was removed by distillation at ordinary pressure. The residual liquid was distilled under diminished pressure through a 12-inch column packed with Berl saddles yielding 264.0 g. (93.5%), b.p. 118–123° (1.5 mm.), $n^{25}\text{D}$ 1.4468. The infrared spectrum was identical to that reported in the previous section.

*Anal.* Calcd. for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 67.77; H, 9.30.

The 2,5-diallyladipic acid derivative of the diester was prepared. An analytically pure sample was obtained after five recrystallizations from very dilute ethanol solution; m.p. 102–104°. An infrared spectrum (Nujol) was consistent with the expected structure.

*Anal.* Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.75; H, 8.06.

**Ethyl Hydrogen 2,5-Diallyladipate (VI).**—The partial saponification of diethyl 2,5-diallyladipate was accomplished in a manner similar to that described by Fieser and Leffler[15] for the partial saponification of diethyl α-methylpimelate.

A solution of 353.0 g. (1.25 moles) of diethyl 2,5-diallyladipate (V), 1 l. of absolute ethanol and 81.23 g. (1.25 moles) of 86.3% potassium hydroxide dissolved in 600 ml. of absolute ethanol was stirred in a stoppered flask with a magnetic stirrer at room temperature for three days, then concentrated to approximately 400 ml. by distillation of the solvent at reduced pressure on a steam-bath; 1.5 l. of water was added and the mixture extracted with three 200-ml. portions of ether so as to remove the unchanged diester starting material. (Evaporation of the ether extracts followed by distillation of the remaining oil yielded 70.0 g. of diester.) Acidification of the aqueous solution with ice-cold 18% hydrochloric acid gave an oily organic layer which was separated by extraction of the aqueous mixture with three 300-ml. portions of benzene. After removing the benzene by distillation at ordinary pressure, the remaining liquid was distilled at reduced pressure through a 12-inch Vigreux column yielding 197.1 g. (77.5% calculated on the basis of unrecovered diester starting material), b.p. 132–137° (0.06 mm.), $n^{25}\text{D}$ 1.4598 (40 g. of crude diacid was also recovered). The infrared spectrum contains bands assignable to an aliphatic acid (3250, 2685 and 1715 cm.$^{-1}$), to an aliphatic ester (1735, 1188 and 1165 cm.$^{-1}$), and to a terminal vinyl group (1648, 1000 and 920 cm.$^{-1}$).

*Anal.* Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.70; H, 8.94.

**2,5-Diallyladipamic Acid (VII).**—In a tightly stoppered flask were placed 5.00 g. (0.02 mole) of ethyl hydrogen 2,5-diallyladipate (VI), 25 ml. of concentrated ammonium hydroxide and a trace of ammonium chloride. The flask was allowed to stand at room temperature for six months. After cooling the solution in an ice–salt-bath, ice-cold concentrated sulfuric acid was added slowly with stirring to the congo red end-point. A white crystalline material separated and was isolated by filtration yielding 2.35 g. (53%), m.p. 126–138°. The product was recrystallized three times from water giving an analytically pure sample, m.p. 155–157°. The infrared spectrum (Nujol) contains bands assignable to an aliphatic acid (2520, 1705 cm.$^{-1}$), to an aliphatic amide (3345, 3165 and 1667 cm.$^{-1}$), and to a terminal vinyl group (1650, 1000 and 920 cm.$^{-1}$).

*Anal.* Calcd. for $C_{12}H_{19}NO_3$: C, 63.97; H, 8.50; N, 6.22. Found: C, 64.03; H, 8.51; N, 6.07.

**Ethyl 2,5-Diallyladipoylate Chloride (VIII).**—The method is essentially that which Horowitz and Geissmann[16] used in the preparation of α-allylphenylacetyl chloride from the corresponding acid. A mixture of 127.2 g. (0.50 mole) of ethyl hydrogen 2,5-diallyladipate (VI), 39.5 g. (0.50 mole) of dry pyridine and 500 ml. of dry ether was stirred while 59.5 g. (0.50 mole) of specially purified thionyl chloride[17] dissolved in 60 ml. of dry ether was added in a dropwise manner. A white precipitate of pyridine hydrochloride formed immediately. The mixture was stirred continuously at room temperature for 16 hours. The liquid was then separated from the solid by decantation and the solvent, ether, removed under reduced pressure. A yield of 129 g. (94.6%) of crude product was obtained. (The bulk of the product was not purified further since it was to be used directly in the subsequent preparation of ethyl 2,5-diallyladipamate (IX).) A small sample was withdrawn and subjected to a fractional distillation through a 10-inch Vigreux column under diminished pressure yielding an analytically pure sample, b.p. 106° (0.8 mm.), $n^{20}\text{D}$ 1.4651. The infrared spectrum contains bands assignable to an aliphatic ester (1735, 1185 cm.$^{-1}$), to an acid chloride (1795 cm.$^{-1}$), and to a terminal vinyl group (1647, 1000 and 925 cm.$^{-1}$).

*Anal.* Calcd. for $C_{14}H_{21}O_3Cl$: C, 61.64; H, 7.76. Found: C, 61.21; H, 7.81.

**Ethyl 2,5-Diallyladipamate (IX).**—One hundred and twenty-nine grams (0.47 mole) of ethyl 2,5-diallyladipoylate chloride (VIII) was added dropwise with stirring to 1 l. of ice-cold concentrated ammonium hydroxide solution. An oily product separated and was isolated by extraction with one 300-ml. and two 100-ml. portions of ether. Evaporation of the ether solvent followed by complete drying in a vacuum desiccator yielded 105 g. (88%), $n^{20.5}\text{D}$ 1.4772. Distillation of a small sample of the product at reduced pressure through a 10-inch Vigreux column yielded an analytically pure sample, b.p. 145–148° (0.05 mm.), $n^{20}\text{D}$ 1.4783. The infrared spectrum contains bands assignable to an aliphatic ester (1733, 1192 cm.$^{-1}$), to an amide (3440, 3350, 3200 and 1670 cm.$^{-1}$), and to a terminal vinyl group (1650, 1000 and 920 cm.$^{-1}$).

*Anal.* Calcd. for $C_{14}H_{23}NO_3$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.16; H, 9.20; N, 5.40.

Upon standing, 1.3 g. of the 2,5-diallyladipamide derivative separated from the above ammonium hydroxide extracts. After two recrystallizations from dilute ethanol an analytically pure sample was obtained, m.p. 230–231°. An infrared spectrum (Nujol) was consistent with the proposed structure.

*Anal.* Calcd. for $C_{12}H_{20}N_2O_2$: C, 64.25; H, 8.99; N, 12.49. Found: C, 64.52; H, 9.02; N, 12.27.

**Preparation of Monomer (X) *via* the Hofmann Reaction.**—To a solution of 30.67 g. (1.33 g. atoms) of sodium in 1500 ml. of absolute ethanol, 169.0 g. (0.667 mole) of ethyl 2,5-diallyladipamate (IX) was added. The stirrer was started; the solution heated to near reflux temperature and then 106.7 g. (0.667 mole) of bromine was introduced in a dropwise manner over a period of two hours. After the bromine addition was complete, the reaction mixture was heated under reflux with stirring for two more hours. The mixture, which contained precipitated sodium bromide, was cooled, transferred to a 2-l. distillation flask, neutralized with a few drops of concentrated hydrochloric acid, and then evaporated to approximately 500 ml. at reduced pressure. The residual liquid was diluted with 2.5-l. of water, stirred thoroughly and extracted with one 400-ml. portion and two 200-ml. portions of ether. The combined ethereal extracts were evaporated to dryness under diminished pressure. Fractionation of the residual liquid under diminished pressure through a 12-inch Vigreux column yielded the following: I, 9.30 g., b.p. 143–154° (0.4 mm.), $n^{20}\text{D}$ 1.4642; II, 53.05 g., b.p. 152–160° (0.35 mm.), $n^{20}\text{D}$ 1.4676; III, 5.04 g., b.p. 148–154° (0.12 mm.), $n^{20}\text{D}$ 1.4738; IV, 46.06 g., b.p. 155–165° (0.15 mm.), $n^{20}\text{D}$ 1.4752.

Fractions I and II were combined and refractionated at reduced pressure through a 10-inch Vigreux column yielding the following: 1, 4.20 g., b.p. 100–120° (0.05 mm.), $n^{20}\text{D}$ 1.4611; 2, 42.69 g., b.p. 120–123° (0.05 mm.), $n^{20}\text{D}$ 1.4651; 3, 9.10 g., b.p. 123–125° (0.05 mm.), $n^{20}\text{D}$ 1.4697; 4, 5.05 g., b.p. 140–145°, (0.05 mm.), $n^{20}\text{D}$ 1.4771.

Considering fractions 1, 2 and 3 as monomer X, 56 g., and fractions III, IV and 4 as amide starting material, 56.15 g., a yield of 42.1% was realized calculated on the basis of unrecovered starting material. The infrared spectrum contains bands assignable to an aliphatic ester (1732, 1250 and 1183 cm.$^{-1}$), to a carbamate (3350, 1715, 1698 and 1675 cm.$^{-1}$), and to a terminal vinyl group (1650, 1000 and 920 cm.$^{-1}$).

*Anal.* Calcd. for $C_{16}H_{27}NO_4$: C, 64.62; H, 9.15; N, 4.71. Found (Fraction 2): C, 64.33; H, 9.08; N, 4.87.

**Emulsion Polymerization of Monomer X and Hexamethylenedithiol.**—The emulsifier–buffer solution of the compo-

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[15] L. F. Fieser, M. T. Leffler, *et al.*, THIS JOURNAL, **70**, 3208 (1948).

[16] R. M. Horowitz and T. A. Geissmann, THIS JOURNAL, **72**, 1518 (1950).

[17] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p. 185.

sition 2% MP-635-S,[18] 0.5% Daxad-11,[19] *p*H 3.5, and 2 *M* sodium acetate was prepared the day immediately preceding polymerization and was stored under nitrogen in a tightly stoppered flask. The initiator–activator solution was freshly prepared on the day of polymerization by dissolving 2.150 g. of ammonium persulfate, 1.108 g. of sodium bisulfite and 0.110 g. of cupric sulfate pentahydrate in redistilled, oxygen-free water and diluting to a volume of 100 ml. Four-ounce screw-cap bottles fitted with self-sealing GR-A rubber gaskets which had previously been flushed with nitrogen were used for polymerizations.

Monomer charges were prepared by weighing equimolar quantities of monomers, 40.0000 g. (0.1345 mole) of monomer X and 20.2171 g. (0.1345 mole) of freshly distilled hexamethylenedithiol, into a flask. After swirling gently for 15 minutes, in order to assure complete homogeneity, 5-ml. aliquots (*ca.* 4.7 g.) were withdrawn and added to the polymerization bottles containing 50 ml. of emulsifier–buffer solution and 1 ml. of initiator–activator solution. The bottles were then sealed, capped tightly, and tumbled end-over-end in a 30° constant temperature bath for five days. The latices were coagulated by pouring into 20 ml. of alum coagulant solution prepared by dissolving 100 g. of potassium aluminum sulfate in a solution of 100 ml. of concentrated hydrochloric acid and 1 l. of distilled water. The polymers were isolated by decantation and then washed by decantation with one 50-ml. portion of water and three 50-ml. portions of a 40–10 methanol–water solution. The samples were dried in a vacuum desiccator until a constant weight was obtained.

Inherent viscosities were determined by means of a modified Ostwald viscometer at 25° using 0.200-g. samples dissolved in 50 ml. of chloroform. Polymer was obtained with inherent viscosities from 0.09 to 0.13.

An analytically pure polymer was obtained by dissolving a sample of the crude polymer in 10 ml. of chloroform, filtering through a 100-mesh stainless steel screen and reprecipitating by pouring the solution into a solution of 90 ml. of methanol and 10 ml. of water. The reprecipitated polymer was isolated by decantation and dried under diminished pressure (0.5 mm.) for three days in an Abderhalden vacuum drying apparatus heated to 80°. The polymer thus obtained had an inherent viscosity of 0.134. The infrared spectrum (chloroform) contains bands assignable to an aliphatic ester and ethyl carbamate (1708–1720, 1210–1240 cm.$^{-1}$) and to a carbamate N–H (3420 cm.$^{-1}$).

*Anal.* Calcd. for $C_{22}H_{41}NO_4S_2$: C, 59.02; H, 9.23; S, 14.32. Found: C, 59.02; H, 9.03; S, 14.62.

**Hydrolysis of Polymer XI to Polyampholyte XII.**—Four and four-tenths grams of polymer XI having an inherent viscosity of 0.103 was dissolved in 25 ml. of redistilled benzene and placed in a 100-ml. platinum dish. To this solution was added 50 ml. of distilled water and 10.0 g. of sodium hydroxide. The dish was placed in drying oven heated to 60° overnight in an effort to remove the benzene. The dish was then covered with a watch glass, and placed in an autoclave, where it was heated to approximately 125° in a pressure of 24 p.s.i. for eight days. The product was obtained in the form of a partially soluble soap-like oil. Addition of distilled water brought about almost complete water solubility. The water dispersion was filtered through fluted filter paper, the filter paper was washed several times with water, and the combined filtrate and washings were cooled in an ice-bath. The solution was neutralized slowly with constant rapid stirring with very dilute ice-cold hydrochloric acid. A cloudiness began to appear at a *p*H 9. An emulsion-like product was obtained at a *p*H 6. The suspension was diluted to about 600 ml. with water, transferred to dialysis bags and dialyzed for three days. The dialyzed, salt-free product was then transferred to a 1-l. flask and lyophilized to dryness. The product was obtained in the form of a white, fluffy powder which is soluble in wet tetrahydrofuran, 50–50 dioxane–water and anhydrous sulfuric acid. A yield of 3.2 g. (94%) was recovered, m.p. 104–108°. The infrared spectrum (Nujol) contains bands assignable to an amine N–H (3160, 2700 cm.$^{-1}$), to an acid (2700, 1690 cm.$^{-1}$), to a zwitterion (1645–1655 cm.$^{-1}$) and to an $-NH_3^+$ group (1550 cm.$^{-1}$).

*Anal.* Calcd. for $C_{17}H_{33}NO_2S_2$: C, 58.74; H, 9.57; N, 4.03. Found: C, 58.70; H, 9.70; N, 3.75.

URBANA, ILLINOIS

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[18] This is a mixed sixteen carbon sodium alkane-sulfonate emulsifier obtained from Dr. Stanley J. Detrick, E. I. du Pont de Nemours and Co.

[19] Obtained from Dewey and Almy, Cambridge, Mass. It is a polymerized sodium salt of an alkyl aryl sulfonic acid.

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# Cyclopropene. I. The Reaction of 2-Bromocyclopropanecarboxylates with Potassium *t*-Butoxide

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The reaction of ethyl 2-bromocyclopropanecarboxylate with potassium *t*-butoxide in *t*-butyl alcohol gave ethyl 2-*t*-butoxycyclopropanecarboxylate instead of ethyl cyclopropenecarboxylate. The reaction was shown to involve loss of hydrogen bromide followed by Michael addition of *t*-butyl alcohol by effecting the reaction in a deuterium labeled solvent. Evidence is also presented that the vinyl hydrogen in the intermediate unsaturated ester is sufficiently acidic to exchange easily with the solvent in the presence of potassium *t*-butoxide.

Many investigations have dealt with the effect of "ring strain" on the properties of cyclopropene and related compounds.[2] It should be possible to obtain further useful information on this subject by studying compounds which are more "strained" than cyclopropane, since the unsaturated properties then should become even more prominent. One compound of this type is cyclopropene.[3]

If one considers the model of cyclopropane which has been proposed by Coulson and Moffitt[4] and by Walsh,[5] it would appear that the introduction of a double bond into the molecule would lead to the development of some acetylenic character. This is particularly interesting because of the relatively large difference in properties between the alkenes and the alkynes, as for example in their acidity. In this connection, the corresponding acid cyclopropenecarboxylic acid is also of interest, since whereas butyric and crotonic acids have

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[1] Taken from part of a thesis submitted by R. K. Barnes to the University of Washington in partial fulfillment of the requirements of the Ph.D. degree, 1955. Shell Oil Co. fellow 1953–1954.

[2] *Cf.* E. Vogel, *Fortschr. Chem. Forsch.*, **3**, 430 (1955).

[3] N. J. Demjanov and M. Dojarenko, *Ber.*, **56**, 2200 (1923); M. J. Schlatter, THIS JOURNAL, **63**, 1733 (1941); K. B. Wiberg, Abst. 131st National Meeting, American Chemical Society, Miami, Florida, 1957, p. 39–40.

[4] C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).

[5] A. D. Walsh, *Nature*, **159**, 164 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949).