

current dimerization of the latter, has been reported. Hence one might have anticipated that anthracene would undergo copolymerization reactions.

Experimental

Preparation of Copolymers of Anthracene and 1,3-Butadiene.—A two-ounce screw-capped bottle provided with a rubber gasket was charged with 17.5 ml. of a 2.8% solution of a sodium fatty-acid soap (Office of Synthetic Rubber specifications), 1 ml. of a 3% aqueous solution of potassium persulfate, 0.5 g. of anthracene, 5 ml. of benzene, 0.025 g. of lauryl mercaptan and 12 g. of liquid butadiene (Phillips research grade). The air was swept out of the polymerization bottle by allowing the butadiene to evaporate until the charge contained 9.5 g. of butadiene. The bottle was then sealed and tumbled end-over-end at 50° in a constant-temperature bath for 11 hours. At that time the polymer which had formed was precipitated by adding 5 ml. of a saturated methanol solution of N-phenyl-β-naphthylamine and 5 ml. of a 13% solution of sulfuric acid saturated with sodium chloride. The polymer was washed thoroughly with water and dried in a desiccator under reduced pressure. The product was soluble in benzene and the conversion was 25%. This material was twice redissolved in carbon disulfide and precipitated with acetone. The inherent viscosity in benzene was 1.53.

Absorption Spectra.—One sample of the above copolymer was reprecipitated seven times by making a solution in carbon disulfide and pouring it into acetone. Another sample was reprecipitated ten times in this manner. These samples were dried under reduced pressure. Solutions in cyclohexane having a concentration of 8.5 g. of polymer per liter were examined on a Cary recording spectrophotometer, Model 11, using a 1.0-cm. cell. The absorbance at 2645 Å. was higher than at 2575 and at 2720 Å.

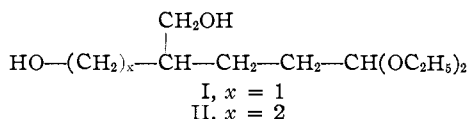
NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

Synthesis and Polymerization of 6-Hydroxy-4-hydroxymethylhexanal Diethyl Acetal and 5-Hydroxy-4-hydroxymethylpentanal Diethyl Acetal¹

By C. S. MARVEL AND JOHN J. DRYSDALE

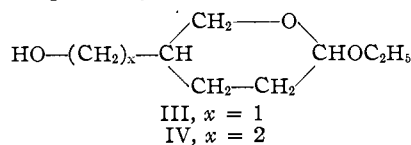
RECEIVED JUNE 15, 1953

The dihydroxyacetals, 5-hydroxy-4-hydroxymethylpentanal diethyl acetal (I) and 6-hydroxy-4-hydroxymethylhexanal diethyl acetal (II), have been polymerized to give low molecular weight,

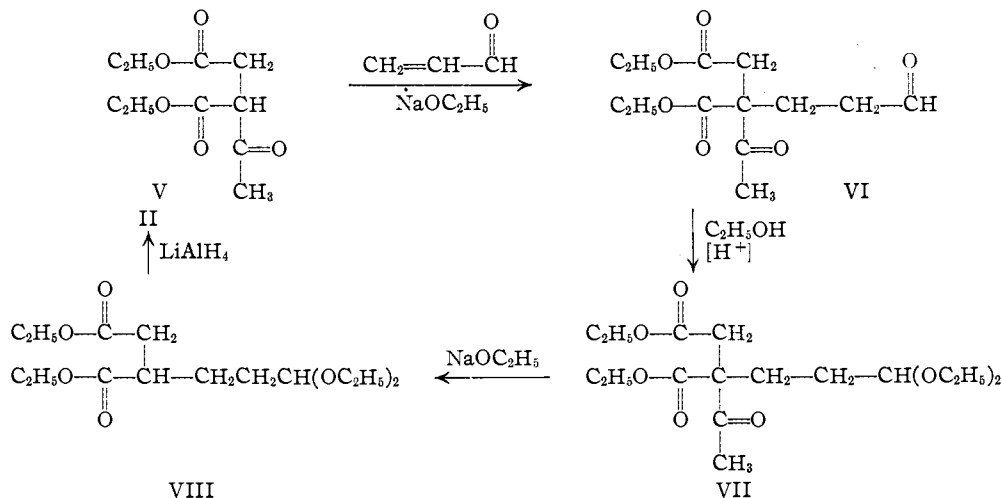


(1) A portion of the work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

soluble polymers. Attempts to increase the molecular weights of the polymeric acetals have been unsuccessful and have led to the formation of gel. The cyclic acetals, 2-ethoxy-5-hydroxymethyl-tetrahydropyran (III) and 2-ethoxy-5-(β-hydroxyethyl)-tetrahydropyran (IV), were isolated from the polymerization mixtures of the dihydroxyacetals, I and II, respectively.



6-Hydroxy-4-hydroxymethylhexanal diethyl acetal (II) was synthesized by the method outlined below.



Experimental²

5-Hydroxy-4-hydroxymethylpentanal Diethyl Acetal (I).—Compound I was synthesized by the method of Marvel and Hill,³ b.p. 113–114° (0.06 mm.), n_D^{20} 1.4532. Infrared analysis in chloroform showed a hydroxyl band at 3378 cm^{-1} .

α-Acetyl-α-(3,3-diethoxypropyl)-succinic Acid Diethyl Ester (VII).—One gram (0.043 mole) of sodium was dissolved in 1 liter of absolute ethanol in a 2-liter, 3-necked flask equipped with stirrer, reflux condenser and dropping funnel. Two hundred grams (0.92 mole) of diethyl α-acetylsuccinate was added and the ethanolic mixture was cooled to 0°. Stirring was started and 56 g. (1.0 mole) of acrolein was added dropwise over a period of 1 hour. The basic mixture was allowed to stir at 0° for a total of 3 hours. It was then acidified with dry hydrogen chloride and was allowed to stir for 2 more hours.

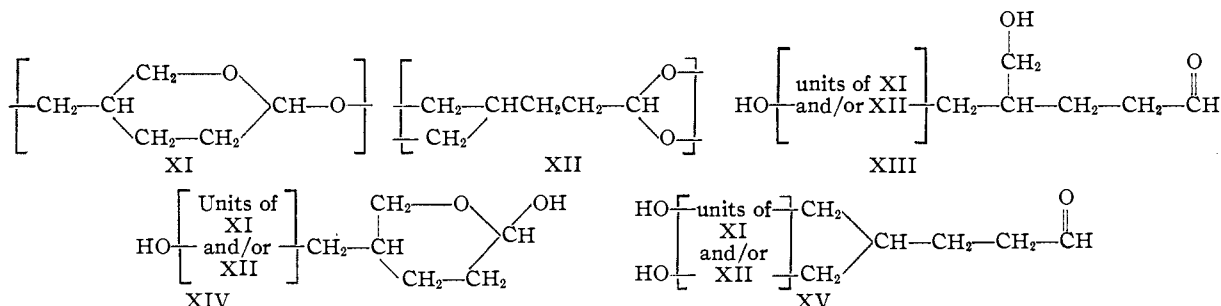
The mixture was neutralized with sodium bicarbonate, diluted with water, and extracted with ether. After removal of the ether at water-pump pressure, the residue was fractionated to give 132 g. of α-acetyl-α-(3,3-diethoxypropyl)-succinic acid diethyl ester (VII), b.p. 157–158° (1.3 mm.), n_D^{20} 1.4520, d_4^{25} 1.068.

Anal. Calcd. for $\text{C}_{17}\text{H}_{30}\text{O}_7$: C, 58.93; H, 8.73. Found: C, 58.90; H, 8.39.

α-(3,3-Diethoxypropyl)-succinic Acid Diethyl Ester (VIII).—One hundred and thirty-two grams (0.38 mole) of compound VII was refluxed with 3.0 g. (0.044 mole) of sodium ethoxide in 1 liter of absolute ethanol for 2.75 hours. The mixture was chilled, neutralized with sodium bicarbonate, filtered, and the ethanol removed at water-pump pressure.

(2) Analyses were performed by Mrs. Katherine Pih, Mrs. Jean Fortney, Mrs. Lucy Chang and Jozsef Nemeth of the University of Illinois Microanalytical Laboratory. Infrared analyses were performed by Mrs. Elizabeth Leighly of the University of Illinois and by the Anderson Physical Laboratories, Champaign, Ill.

(3) C. S. Marvel and H. W. Hill, Jr., *THIS JOURNAL*, **73**, 481 (1951).



Distillation of the residue gave 58 g. (50%) of α -(3,3-diethoxypropyl)-succinic acid diethyl ester (VIII), b.p. 157–158° (3.8 mm.), n_D^{20} 1.4370–1.4378, d_4^{25} 1.022.

6-Hydroxy-4-hydroxymethylhexanal Diethyl Acetal (II).—Fifty-eight grams (0.19 mole) of compound VIII was reduced with 10 g. (0.0264 mole) of lithium aluminum hydride, according to the procedure of Marvel and Hill,³ to give 31.5 g. (75%) of 6-hydroxy-4-hydroxymethylhexanal diethyl acetal, b.p. 152–153° (1 mm.). A small sample was distilled from sodium carbonate and analyzed, b.p. 131° (0.06 mm.), n_D^{20} 1.4610. Infrared analysis in chloroform showed a hydroxyl band at 3336 cm.⁻¹.

Anal. Calcd. for C₁₁H₂₄O₄: C, 59.97; H, 10.98. Found: C, 60.20; H, 10.70.

2-Ethoxy-5-hydroxymethyltetrahydropyran (III).—When 5-hydroxy-4-hydroxymethylpentanal diethyl acetal was polymerized (see below) at temperatures above 100° (1.5 mm.), a clear white liquid, 2-ethoxy-5-hydroxymethyltetrahydropyran, distilled from the reaction mixture, b.p. 95–97° (1.5 mm.), n_D^{20} 1.4563. Infrared analysis showed a hydroxyl group (3418 cm.⁻¹) and the absence of an aldehyde group.

Anal. Calcd. for C₈H₁₆O₃: C, 59.98; H, 10.60. Found: C, 60.25; H, 10.36.

2-Ethoxy-5-(β -hydroxyethyl)-tetrahydropyran (IV).—A small sample of 6-hydroxy-4-hydroxymethylhexanal diethyl acetal was heated at reduced pressure for a short time and then fractionated to give a polymeric residue and a colorless liquid, 2-ethoxy-5-(β -hydroxyethyl)-tetrahydropyran (IV), b.p. 97° (1.6 mm.), n_D^{21} 1.4602. Infrared analysis on the pure liquid showed a hydroxyl band at 3418 cm.⁻¹.

Anal. Calcd. for C₈H₁₆O₃: C, 62.03; H, 10.41. Found: C, 62.06; H, 10.52.

Polymerization of Compound I.—One gram of 5-hydroxy-4-hydroxymethylpentanal diethyl acetal (I), n_D^{20} 1.4530–32, was placed in a small tube connected with a distillation system, a small crystal of *p*-toluenesulfonic acid monohydrate was added, the pressure in the distillation system was reduced to 0.02 mm., and heat was applied by means of an oil-bath. The bath temperature was kept slightly below the reflux temperature of the cyclic acetal III until the reaction mixture became quite viscous. The bath temperature was then raised to 120° and heating was continued for a total of 15 minutes. The reaction mixture was cooled, neutralized with concentrated ammonia, and extracted with chloroform. The chloroform extract was decolorized with Darco and evaporated to dryness under reduced pressure. The average molecular weight of the polymer as determined in bornyl bromide was 1190 \pm 100; inherent viscosity in chloroform was 0.14. Infrared analysis of a film of the polymer showed a hydroxyl absorption at 3440 cm.⁻¹ and a carbonyl absorption at 1736 cm.⁻¹. The polymer softened at 49° to give a transparent glass.

Anal. Calcd. for (C₈H₁₆O₂)₇₂(C₈H₁₂O₃)₃₂: C, 60.29; H, 8.93. Found: C, 60.28; H, 8.67.

The above data are consistent with a branched structure whose internal C₈H₁₆O₂ units may have structure XI and/or XII and whose end C₈H₁₂O₃ units may have structure XIII, XIV and/or XV, and in which the average ratio of internal to external units is 7/3.

Polymerization of compound I in the above manner with a reaction time of 2 hours produced a polymer which was approximately 80% insoluble in chloroform; inherent viscosity in chloroform of the soluble portion, 0.17.

Polymerization of II.—Five grams of the dihydroxy acetal (II) was placed in a 25-ml. pear-shaped flask and the flask

attached to a small distillation system. The system was evacuated to 1 mm. and the flask immersed in an oil-bath maintained at 210–220°. After 27 hours, heat was applied to the distillation column and a small amount of the cyclic acetal IV removed. A sample of material removed from the reaction flask at this time had an inherent viscosity in chloroform of 0.04.

The reaction flask was heated for 24 hours more at 210–220° (39 mm.) to give a firm, light red, translucent solid, inherent viscosity in chloroform 0.10. Continued heating in the above manner failed to raise the observed viscosity but did produce increasing amounts of gel. This polymer was assumed to contain a branched structure and structural units similar to the polymeric acetal I.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

Synthesis of 3,5-Dibromophenylsilanes

BY C. R. MORGAN, H. A. HOFFMAN AND F. E. GRANCHELLI
RECEIVED APRIL 10, 1953

In the course of an investigation of organosilanes of high density it became of interest to attempt the conversion of 1,3,5-tribromobenzene to 3,5-dibromophenylsilane derivatives. Following a brief unsuccessful effort to prepare a Grignard reagent from the tribromobenzene, we decided to employ 3,5-dibromophenyllithium (I) for reaction with the chlorosilanes. Gilman had reported¹ a 56% yield of 3,5-dibromobenzoic acid upon carbonation of the dibromophenyllithium compound, but no study was made of the optimum conditions for the halogen-metal interchange between *n*-butyllithium and 1,3,5-tribromobenzene. We have examined the effect of reaction time, as measured by the yield of 3,5-dibromobenzoic acid and find that in ether, with reaction times of 0.5, 1.0, 2.0 and 5.0 minutes, yields of 77, 78, 54 and 38%, respectively, were obtained. In petroleum ether, a one-minute reaction time gave only 18%. From the neutral portion of the reaction mixtures a product melting at 208.5–209° was isolated. This does not appear to correspond to the expected 3,5,3',5'-tetrabromobiphenyl (m.p. 186°), but may be the tetrabromodiphenyl ketone.

Reactions of I were conducted with silicon tetrachloride, dimethyldichlorosilane and methyltrichlorosilane. The accompanying equations illustrate the methods used to prepare the various dibromophenylsilanes employing a one-minute reaction time for preparation of the lithium reagent. Yields of the tetrasubstituted silanes generally were good, but difficulties were encountered in con-

(1) H. Gilman, W. Langham and F. W. Moore, *THIS JOURNAL*, **62**, 2327 (1940).