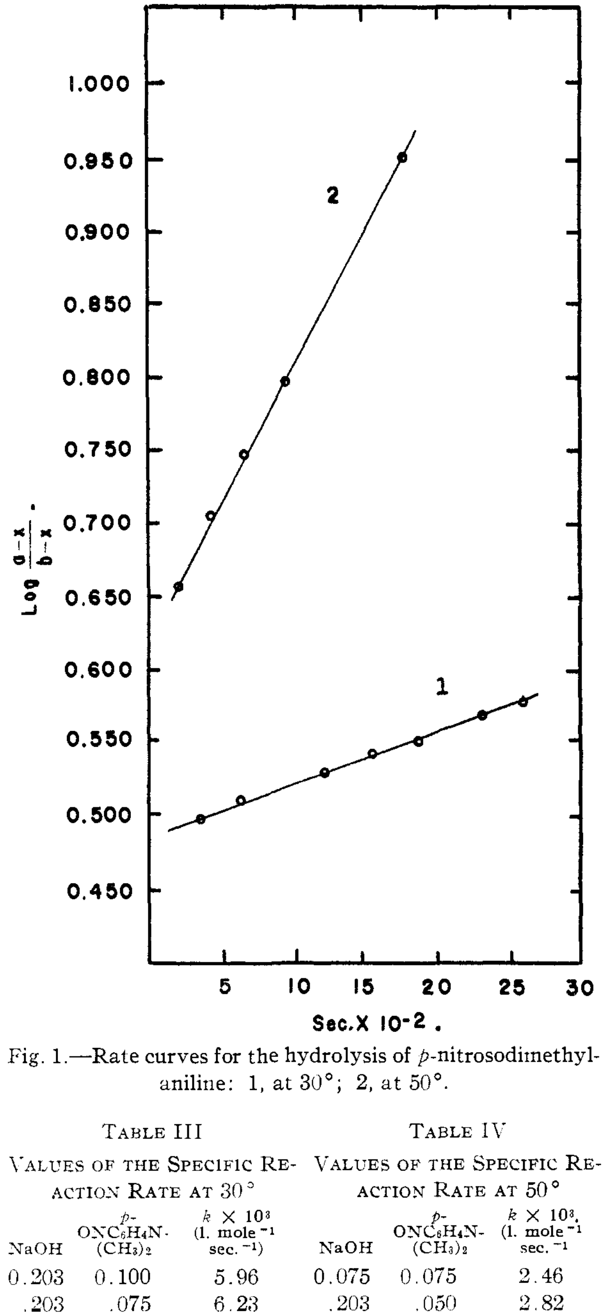

Fig. 1.—Rate curves for the hydrolysis of *p*-nitrosodimethylaniline: 1, at 30°; 2, at 50°.

TABLE III

VALUES OF THE SPECIFIC REACTION RATE AT 30°

NaOH	*p*-$ONC_6H_4N(CH_3)_2$	$k \times 10^3$ (l. mole^{-1} sec.$^{-1}$)
0.203	0.100	5.96
.203	.075	6.23
.102	.095	7.27
.143	.085	7.51
.203	.050	7.16
	Av.	6.4 ± 0.7

TABLE IV

VALUES OF THE SPECIFIC REACTION RATE AT 50°

NaOH	*p*-$ONC_6H_4N(CH_3)_2$	$k \times 10^3$, (l. mole^{-1} sec.$^{-1}$
0.075	0.075	2.46
.203	.050	2.82
.199	.050	2.58
.203	.070	2.20
.199	.090	2.10
	Av.	2.4 ± 0.4

agreement with similar data for known aromatic nucleophilic displacement reactions.[2c] Therefore, the cleavage of *p*-nitrosodimethylaniline may now be considered as an example of this reaction type, and the mechanism of the reaction may be thought of as that of a typical aromatic nucleophilic displacement reaction,[2] although, as pointed out by Berliner,[7] it is not yet possible to decide whether the formation or decomposition of the transition complex is the rate determining step. It is noteworthy that the values of the activation energy and log *PZ* for this reaction, in comparison with those for other reactions of this type, substantiate the statement of LeFevre[8] that one nitroso group will activate a group toward displacement roughly to the same extent as two nitro groups.

[7] E. Berliner and L. C. Monack, THIS JOURNAL, **74**, 1574 (1952).

[8] R. J. W. LeFevre, *J. Chem. Soc.*, 810 (1931).

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Copolymerization of Anthracene with 1,3-Butadiene[1]

BY C. S. MARVEL AND W. S. ANDERSON

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Recently Stockmayer and Peebles demonstrated the ability of benzene to copolymerize with vinyl acetate.[2] This prompts us to record the copolymerization of another aromatic hydrocarbon, anthracene, with 1,3-butadiene.

Copolymers prepared from butadiene (95 pts.) and anthracene (5 pts.) in the Mutual recipe[3] showed an intense ultraviolet absorption with maxima at 2575, 2645 and 2720 Å. which were not altered by repeated solution and reprecipitation of the copolymer. These absorption peaks resemble very closely those reported for 9,10-dihydroanthracene[4a] and for 9,10-dimethyl-9,10-dihydroanthracene,[4b] which indicates that the copolymerization involves the 9,10-positions in the anthracene molecule. Using the extinction coefficients for 9,10-dihydroanthracene for comparison, it is calculated that approximately 5% by weight of anthracene has been incorporated in a copolymer prepared to 25% conversion.

Agitation of anthracene with polybutadiene latex does not produce a polymer with these absorption maxima; hence the anthracene is not introduced by an addition to the polybutadiene.

Benzene was employed as a mutual solvent for butadiene and anthracene in these emulsion polymerizations. There were no absorption maxima which indicated incorporation of benzene units in the copolymer when anthracene was present or absent during such polymerizations.

That anthracene does give free-radical reactions has been demonstrated before. 2-Methylanthracene has been shown to copolymerize with styrene.[5] Anthracene itself inhibits the autoxidation of benzaldehyde.[6] The photodimerization of anthracene is well known,[7] and recently[8] the addition of free radicals to anthracene, both with and without con-

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[1] 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.

[2] W. H. Stockmayer and L. H. Peebles, Jr., THIS JOURNAL, **75**, 2279 (1953).

[3] J. W. Wilson and E. S. Pfau, *Ind. Eng. Chem.*, **40**, 530 (1948).

[4] (a) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951; (b) G. M. Badger, M. L. Jones and R. S. Pearce, *J. Chem. Soc.*, 1700 (1950).

[5] M. Magat and R. Bonême, *Compt. rend.*, **232**, 1657 (1951).

[6] H. L. J. Backstrom and H. A. Beatty, *J. Phys. Chem.*, **35**, 2530 (1931); G. E. K. Branch, H. J. Almquist and E. C. Goldsworthy, THIS JOURNAL, **55**, 4052 (1933).

[7] F. Fritzsche, *J. prakt. Chem.*, [1] **101**, 337 (1867).

[8] A. F. Bickel and E. C. Kooyman, *Rec. trav. chim.*, **71**, 1137 (1952).

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.

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Synthesis and Polymerization of 6-Hydroxy-4-hydroxymethylhexanal Diethyl Acetal and 5-Hydroxy-4-hydroxymethylpentanal Diethyl Acetal[1]

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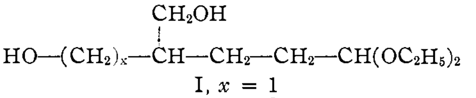
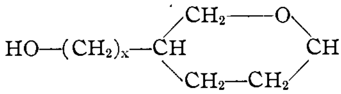
The dihydroxyacetals, 5-hydroxy-4-hydroxymethylpentanal diethyl acetal (I) and 6-hydroxy-4-hydroxymethylhexanal diethyl acetal (II), have been polymerized to give low molecular weight, soluble polymers. Attempts to increase the molecular weights of the polymeric acetals have been unsuccessful and have led to the formation of gel. The cyclic acetals, 2-ethoxy-5-hydroxymethyltetrahydropyran (III) and 2-ethoxy-5-(β-hydroxyethyl)-tetrahydropyran (IV), were isolated from the polymerization mixtures of the dihydroxyacetals, I and II, respectively.



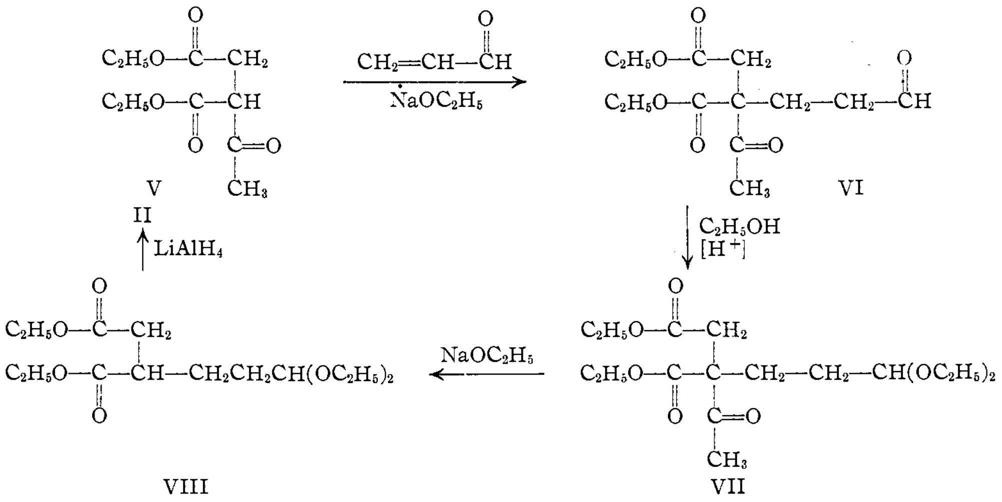
$$\mathrm{HO{-}(CH_2)_x{-}\overset{\displaystyle CH_2OH}{CH}{-}CH_2{-}CH_2{-}CH(OC_2H_5)_2}$$

I, $x = 1$
II, $x = 2$



III, $x = 1$
IV, $x = 2$

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



Experimental[2]

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^{20}_D 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^{20}_D 1.4520, d^{31}_4 1.068.

Anal. Calcd. for $C_{17}H_{30}O_7$: 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.

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[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.

[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).