

*Anal.* Calcd. for  $C_{10}H_{18}O_4$ : neut. equiv., 87. Found: neut. equiv., 83.

**Methyl 5-Methyl-2,5-hexadienoate.**—A mixture of methyl propiolate (30 g., 0.36 mole) and isobutylene (28 g., 0.50 mole) was heated in a stainless steel shaker tube at 220° for 4 hr. From the viscous reaction mixture there was obtained 2.7 g. of product distilling at 30–94° (2 mm.), almost all of which distilled under 40°. Redistillation gave a major fraction,  $n_D^{25}$  1.4541, which has the probable structure

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}=\text{CH}-\text{COOCH}_3 \\ | \qquad \qquad | \\ \text{CH}_3 \qquad \qquad \text{COOCH}_3 \end{array}$$

The minor fraction was not investigated but probably was the isomeric

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{C}-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2 \\ | \qquad \qquad | \\ \text{CH}_3 \qquad \qquad \text{COOCH}_3 \end{array}$$

*Anal.* Calcd. for  $C_8H_{12}O_2$ : C, 68.7; H, 8.6. Found: C, 69.5; H, 9.1.

The combined infrared, near infrared, and proton resonance spectra are in agreement with the structure having one terminal methylene group. Thus a band at 1.63  $\mu$  in the near infrared at approximate intensity 0.341./mole cm. indicates one terminal methylene group per molecule. The infrared spectrum shows bands at 3.24  $\mu$  (unsaturated CH), 3.36, 3.39, 3.43, 3.51  $\mu$  (saturated CH), 5.78  $\mu$  (carbonyl), 6.03  $\mu$  (C=C), 11.20  $\mu$  ( $\text{CH}_2=\text{C}<$ ), and 7.26  $\mu$  ( $\rightarrow\text{C}-\text{CH}_3$ ). The ultraviolet spectrum shows the absence of conjugated unsaturation.

## Pyrolysis of Esters. XXII. Synthesis of Bisdiene from 2-Hydroxymethyl-1,3-butadiene<sup>1,2</sup>

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A new synthesis of 2-hydroxymethyl-1,3-butadiene was developed starting from commercially available 2-amino-2-ethyl-1,3-propanediol and involving a pyrolysis of an amine oxide as well as the pyrolysis of an ester. When the hydroxymethylbutadiene was treated with vinyl acetate in the presence of a mercuric oxide–boron trifluoride etherate mixture, a 38% yield of bis(2-butadienylmethyl) acetal resulted. Treatment of the hydroxymethylbutadiene with hexamethylene diisocyanate gave a 76% yield of solid bis(2-butadienylmethyl) hexamethylenecarbamate, while treatment with *m*-xylylene diisocyanate gave a 91% yield of solid bis(2-butadienylmethyl) *m*-xylylenecarbamate.

In a research program designed to study polymeric Diels–Alder reactions, a series of bifunctional or bisdienes was required. One of the most interesting starting materials for the production of bisdienes appeared to be 2-hydroxymethyl-1,3-butadiene (I). In a previous paper in this series we reported two syntheses of hydroxymethylbutadiene—one a three-step synthesis starting with dimethyl itaconate and an alternative three-step synthesis starting from triethyl 1,1,2-ethanetricarboxylate. The key step in both these syntheses was the pyrolysis of an ester to produce the intermediate 2-acetoxymethyl-1,3-butadiene (II). Since the over-all yield in either of these two syntheses was not very high, a search for still a third route to hydroxymethylbutadiene was undertaken. Since 2-amino-2-ethyl-1,3-propanediol became commercially available, this polyfunctional compound appeared to be an excellent starting material for the synthesis of the required diene. Since it was shown previously that tertiary amides pyrolyze almost as easily as primary esters,<sup>4</sup> the 2-amino-2-ethyl-1,3-propanediol (III) was converted to the corresponding triacetate IV by treatment with acetic anhydride and sodium acetate. However, when the triacetate IV was pyrolyzed at 510°, a 59% yield of 4-acetoxy-

methyl-4-ethyl-2-methyloxazoline (V) was obtained. The oxazoline V was also prepared directly from the aminodiol III. To illustrate the nature of the reaction, 4-acetoxymethyl-2,4-dimethyloxazoline was prepared in a 58% yield from 2-amino-2-methyl-1,3-propanediol.

To avoid this ring closure, the nitrogen was methylated according to the procedure of Senkus<sup>5</sup> in an over-all yield of 87% by treatment with formaldehyde, followed by catalytic reduction. When the dimethylamino compound VI was treated with acetic anhydride, a 91% yield of the corresponding 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol (VII) was obtained. When the diacetate was treated with peracetic acid, the corresponding amine oxide resulted, but was not isolated. When this amine oxide was pyrolyzed according to the method of Cope, Bumgartner, and Schweizer,<sup>6</sup> a 53% yield of 2-acetoxymethyl-2-buten-1-yl acetate (VIII) was obtained.

Alternative procedures for preparation of the diacetate VIII were less satisfactory. When the dihydroxy compound VI was treated with hydrogen peroxide to produce the corresponding dihydroxyamine oxide, this gave a mixture of diols on pyrolysis. The mixture was not separated but was acetylated directly to give a 50% yield of a mixture of acetates consisting of 85 to 90% of 2-acetoxymethyl-2-buten-1-yl acetate (VIII) and 10

(1) Previous paper in this series, *J. Org. Chem.*, **27**, 1975 (1962).

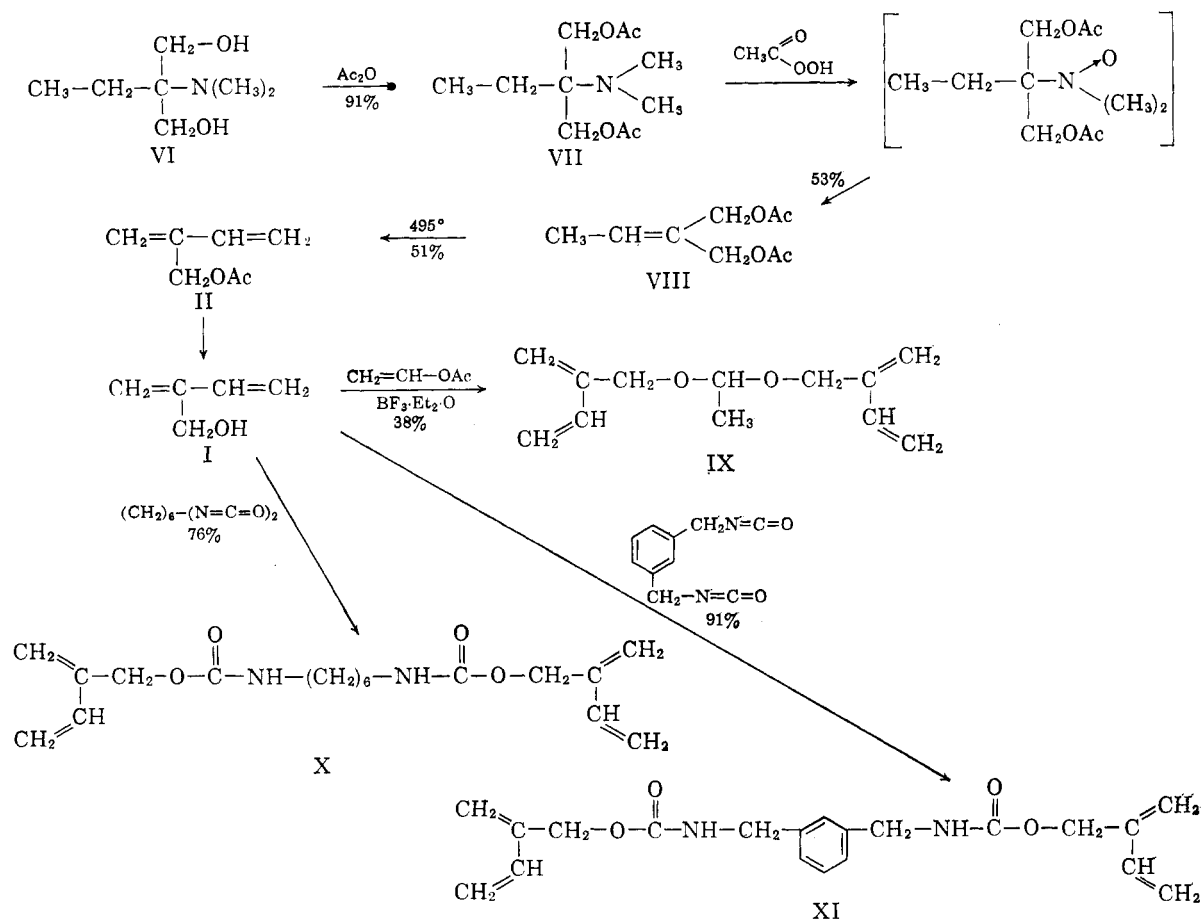
(2) Presented before the Division of Polymer Chemistry at the 138th Meeting of the American Chemical Society, New York, New York, September, 1960.

(3) Office of Naval Research Fellow, 1956–1957; National Science Foundation Fellow, 1957–1959.

(4) W. J. Bailey and C. N. Bird, *J. Org. Chem.*, **23**, 996 (1958).

(5) M. Senkus, *J. Am. Chem. Soc.*, **67**, 1515 (1945).

(6) A. C. Cope, C. L. Bumgartner, and E. E. Schweizer, *ibid.*, **79**, 4729 (1957).



to 15% of presumably the isomeric 2-methylene-1,3-butanediol diacetate. Oxidation of the diacetate VII with 30% hydrogen peroxide resulted in extensive hydrolysis.

Pyrolysis of the diacetate VIII at 495° gave a 34% conversion to 2-acetoxymethyl-1,3-butadiene (II) plus a 33% recovery of a mixture of diacetates. The yield of II, based on unrecovered diacetate, was 51%. It was determined by small scale pyrolysis plus gas chromatography that the yield of the diene II actually decreased as the temperature was increased above 500°. Finally, ester interchange of II with an excess of methanol produced the 2-hydroxymethyl-1,3-butadiene (I), as previously reported.<sup>1</sup>

With the availability of 2-hydroxymethyl-1,3-butadiene (I), it should be possible to prepare a whole series of bifunctional dienes with a wide variety of moieties connecting the two diene systems, and from this series of bifunctional dienes it should be possible to prepare Diels-Alder polymers with widely varying properties. The only practical limitation in the preparation of this series is that only reactions be employed for the coupling process that will not polymerize the diene. One would expect considerable difficulty in purifying high-boiling liquids containing two reactive diene systems. The present work reports a liquid tetraene prepared

by an acid-catalyzed reaction and two solid tetraenes, one prepared under basic conditions and the other under neutral conditions.

The tetraene, bis(2-butadienylmethyl) acetal (IX), was prepared in a 38% yield by the reaction of the 2-hydroxymethyl-1,3-butadiene with vinyl acetate in the presence of a mercuric oxide-boron trifluoride etherate mixture according to the method of Croxall, Glavis, and Neber.<sup>7</sup> (Although these authors indicated that mercuric oxide alone was a milder catalyst, it was not active enough to give any acetal with hydroxymethylbutadiene.) Some insoluble polymer was formed on distillation and the tetraene IX polymerized at room temperature in a few days; however, at -20° compound IX could be stored indefinitely without change.

When two molar equivalents of 2-hydroxymethyl-1,3-butadiene (I) were allowed to stand overnight with hexamethylene diisocyanate with no added catalyst, a 76% yield of bis(2-butadienylmethyl) hexamethylenedicarbamate (X) resulted. Although the solid X did not melt, it softened at 79-80° and formed a cross-linked polymer. On standing at room temperature for 5 days a sample of X became insoluble, but at -20° the solid X was quite stable. Although solid monomers, such as acrylamide and

(7) W. J. Croxall, F. J. Glavis, and H. T. Neber, *J. Am. Chem. Soc.*, **70**, 2805 (1948).

sodium acrylate, have been polymerized,<sup>8</sup> it was surprising to find this tetraene so reactive that it polymerized spontaneously in the solid state at room temperature.

When 2-hydroxymethyl-1,3-butadiene (I) was treated with *m*-xylylene diisocyanate in the presence of triethylenediamine (Dabco), a 91% yield of bis(2-butadienylmethyl) *m*-xylylenedicarbamate (XI) was obtained in one hour. Without the catalyst, several days were required to give a low yield of XI. Again, this solid tetraene did not melt (but polymerized when heated) but could be stored conveniently at  $-20^{\circ}$  with no polymerization.

The use of these interesting bifunctional dienes in Diels-Alder polymerizations will be reported separately.

### Experimental<sup>9</sup>

**2-Amino-2-ethyl-1,3-propanediol Triacetate (IV).**—To 143.5 g. (1.20 moles) of 2-amino-2-ethyl-1,3-propanediol (III) contained in a 1-l. flask were added 378 g. (3.70 moles) of acetic anhydride and 0.5 g. of sodium acetate. The flask was shaken and heat from the spontaneous reaction was dissipated by immersion in an ice bath. After the reaction, which continued for 10 min., had subsided, the mixture was heated for 30 min. on the steam bath. A solution of the resulting oil in 400 ml. of ether was treated with a cold saturated sodium carbonate solution until no additional carbon dioxide was evolved. The aqueous solution was washed with two 50-ml. portions of ether and the ether solutions and the organic layer were combined. After the solution was dried over anhydrous magnesium sulfate, the ether was removed by evaporation. Flash distillation of the residual oil gave 228.2 g. (78%) of impure 2-amino-2-ethyl-1,3-propanediol triacetate (IV), b.p. 110–160° (0.7 mm.). The liquid solidified when cool to a waxy solid, m.p. 40–45°. Further attempts to purify this compound were unsuccessful.

*Anal.* Calcd. for  $C_{11}H_{19}NO_5$ : C, 53.74; H, 7.81. Found: C, 54.78; H, 7.90.

An examination of the infrared spectrum of this compound in carbon tetrachloride solution with a Beckman IR-4 spectrophotometer showed the presence of no bands corresponding to carboxylic acid or hydroxyl groups and peaks at 3360, 1570, 1705, and 1760  $cm^{-1}$ , corresponding to N—H stretching, the "Amide II" band,<sup>10</sup> the amide and acetate carbonyl stretching frequencies, respectively.

**4-Acetoxyethyl-2,4-ethyl-2-methyloxazoline (V).** **A. By Pyrolysis of 2-Amino-2-ethyl-1,3-propanediol Triacetate (IV).**—At a rate of 1.0 g. per minute, 67.0 g. (0.273 mole) of molten 2-amino-2-ethyl-1,3-propanediol triacetate was dropped through a helix-packed Vycor tube, heated externally at 510–520°. Although the pyrolysate, which was collected in a receiver cooled in a Dry Ice–methyl Cellosolve bath, was brown in color, the pyrolysis tube showed little evidence of carbonization. After the product was washed with a cold saturated sodium carbonate solution until no more carbon dioxide was evolved, 100 ml. of ether was added to dissolve the oily layer. The aqueous layer was extracted with two 50-ml. portions of ether, and the combined ether extracts were dried over anhydrous magnesium sulfate. After the ether was removed by evaporation on a steam bath, the

residue was distilled through a 10-in. Vigreux column to yield 30.1 g. (59%) of 4-acetoxyethyl-2,4-ethyl-2-methyloxazoline (V), b.p. 113° (15 mm.),  $n_D^{25}$  1.4450, plus a considerable amount of undistilled residue.

*Anal.* Calcd. for  $C_9H_{15}NO_3$ : C, 58.36; H, 8.16. Found: C, 58.77; H, 8.36.

**B. Direct from 2-Amino-2-ethyl-1,3-propanediol (III).**—When 51 g. (0.43 mole) of 2-amino-2-ethyl-1,3-propanediol (III) (Commercial Solvents Corp.) in a 500-ml. flask was treated with 132 g. (1.24 moles) of acetic anhydride and 0.1 g. of sodium acetate, an immediate reaction ensued, and the solvent refluxed although the flask was immersed in an ice bath. After the mixture had been heated under reflux for 20 min., distillation through a 12-in. Vigreux column gave 15.9 g. (21%) of 4-acetoxyethyl-2,4-ethyl-2-methyloxazoline (V), b.p. 65–66° (0.5 mm.),  $n_D^{25}$  1.4455.

**4-Acetoxyethyl-2,4-dimethyloxazoline.**—To a 500-ml., three-necked flask fitted with an efficient stirrer, a reflux condenser, and a dropping funnel and containing 52.5 g. (0.50 mole) of 2-amino-2-methyl-1,3-propanediol (Commercial Solvents Corp.) was added 360 g. (3.5 moles) of acetic anhydride, first in a 100-ml. portion, which was stirred until the viscous aminodiol went into solution with spontaneous heating, and then slowly to maintain reflux. After the solution was heated under reflux for 2.5 hr., the excess acetic anhydride and the acetic acid were removed by distillation, and the brown residue was distilled through a 12-in. Vigreux column at 15 mm. pressure to give 73.3 g. of an oil, b.p. 90–119°,  $n_D^{25}$  1.4212. However, during the distillation, acetic acid was collected in the Dry Ice trap. Since the boiling range was very wide and acetic acid and other contaminants were present after the first distillation, the product was redistilled to give 49.3 g. (58%) of 4-acetoxyethyl-2,4-dimethyloxazoline, b.p. 99.5–102.5° (15 mm.),  $n_D^{25}$  1.4402.

*Anal.* Calcd. for  $C_8H_{13}NO_3$ : C, 56.12; H, 7.65. Found: C, 56.39; H, 7.45.

**2-(*N,N*-Dimethylamino)-2-ethyl-1,3-propanediol Diacetate (VII).**—The procedure used for the synthesis of 5-ethyl-3,7-dioxo-1-azabicyclo[3.3.0]octane was essentially that of Senkus,<sup>5</sup> modified to enable the use of gaseous formaldehyde. Hydrogenolysis of 236 g. (1.65 moles) of this compound carried out essentially according to the method of Senkus<sup>5</sup> yielded 216.5 g. (89%) of 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol (VI), b.p. 94° (0.5 mm.), m.p. 33° (reported<sup>5</sup> m.p. 32°). To 51.8 g. (0.35 mole) of 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol (VI) in a 250-ml. flask was added 100 ml. of acetic anhydride (approximately a 50% excess). After the spontaneous reaction had subsided, the acetic acid and excess acetic anhydride were removed by distillation under water pump pressure. The residual oil, which contained some insoluble, gummy material, was washed with a cold dilute sodium carbonate solution. After 200 ml. of ether was added, the resulting mixture was filtered to remove a small amount of insoluble material. The ether layer of the filtrate was separated and the aqueous solution was extracted with four 50-ml. portions of ether. After the combined solutions were dried over magnesium sulfate, the ether was removed by distillation and the residual oil was fractionated through a 10-in. Vigreux column to yield 69.5 g. (91%) of 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol diacetate (VII), b.p. 94° (1.0 mm.),  $n_D^{25}$  1.4472.

*Anal.* Calcd. for  $C_{11}H_{21}NO_4$ : C, 57.12; H, 9.15. Found: C, 57.09; H, 8.86.

**2-(*N,N*-Dimethylamino)-2-ethyl-1,3-propanediol Diacetate Hydrobromide.**—To a small sample of the diacetate VII was added 5% solution of bromine in carbon tetrachloride until the red color persisted. After the solvent was removed by evaporation and the residue was dissolved in methanol, the resulting solution was cooled to  $-20^{\circ}$ . Upon the addition of ether to the solution a white powder, 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol diacetate hydrobromide, m.p. 153–156°, soluble in water and giving an

(8) A. Restaino, R. B. Mesrobian, H. Morawetz, D. Ballantine, G. Dienes, and D. Metz, *J. Am. Chem. Soc.*, **78**, 2939 (1956).

(9) The authors are grateful to Mrs. Kathryn Baylouny and Mrs. Jane Ratka for the microanalyses. The infrared absorption spectra were determined on a Beckman IR-5 infrared spectrophotometer.

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 205.

immediate precipitate with a silver nitrate solution, separated.

*Anal.* Calcd. for  $C_{11}H_{22}BrNO_4$ : C, 42.45; H, 6.80. Found: C, 42.32; H, 6.73.

**2-Acetoxyethyl-2-buten-1-yl Acetate (VIII).**—A solution of 0.9 g. of sulfuric acid and 90 ml. of acetic anhydride was dropped slowly into a 250-ml., three-necked flask fitted with a condenser, a dropping funnel, and a magnetic stirrer, containing 18 ml. of 30% hydrogen peroxide by the procedure of Byers and Hickinbottom<sup>11</sup> for the synthesis of solutions of peracetic acid in acetic acid. To this solution were added 2.0 g. of sodium acetate to neutralize the sulfuric acid and then 29 g. (0.125 mole) of 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol diacetate at a rate such that the temperature did not exceed 40°. The solution was stirred at room temperature for 8 hr., and the acetic acid and excess peracetic acid were then removed under reduced pressure so that the temperature of the solution did not rise above 60°.

The apparatus for the pyrolysis of the amine oxide consisted of a Claisen head and a Friedrichs condenser attached to the original 500-ml. flask and leading to a 200-ml., side-armed flask immersed in ice water. The side-arm was connected through a large capacity trap immersed in a Dry Ice-methyl Cellosolve cooling bath to a vacuum pump. At 2-mm. pressure and a temperature of 80–130° decomposition of the oxide and distillation of the products took place with the formation of almost no residue. The oil obtained in the first receiver was washed with 50 ml. of water, the aqueous extract was made basic by the addition of an aqueous sodium carbonate solution until carbon dioxide was no longer evolved, and then this solution was extracted with three 25-ml. portions of ether. After the original organic product and the ether extracts were combined and dried over anhydrous magnesium sulfate, they were distilled, first to remove the ether, and then at low pressure to yield 12.4 g. (53%) of 2-acetoxyethyl-2-buten-1-yl acetate (VIII), b.p. 80° (0.5 mm.),  $n_D^{25}$  1.4438.

*Anal.* Calcd. for  $C_9H_{17}O_4$ : C, 58.05; H, 7.58. Found: C, 58.34; H, 7.63.

Vapor phase chromatography on the silicone grease on Chromosorb column at 207° gave only one peak (which corresponded in retention time to that of the major peak of the product formed by the acetylation of the 2-hydroxyethyl-2-buten-1-ol).

**Oxidation of 2-(*N,N*-Dimethylamino)-2-ethyl-1,3-propanediol (VI) with Hydrogen Peroxide and Pyrolysis of the Amine Oxide.**—In a 500-ml. flask immersed in an ice bath, 216 g. (1.47 moles) of 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol (VI) was treated with 148 g. (1.47 moles) of 30% hydrogen peroxide. After the spontaneous reaction had subsided, the reactants were allowed to stand for a day. Failure of a small portion of this solution to liberate iodine from potassium iodide indicated that there was no excess of hydrogen peroxide. An aliquot of this solution treated with picric acid in ethanol yielded a picrate, m.p. 156–158° (dec.). From the weight of this picrate it was calculated that at least an 81% yield of the amine oxide had been formed. The water was removed under water pump pressure at a temperature not exceeding 60° until the white hygroscopic, solid amine oxide crystallized in the flask.

The pyrolysis was carried out in the apparatus described above at 1 mm. pressure by heating the amine oxide slowly until at about 85° decomposition began with darkening and liquefaction of the amine oxide. Heating was continued until the temperature reached 125° and no more material was distillable. There remained a considerable amount of a black, viscous residue. Most of the dimethylhydroxylamine formed passed into the cold trap while the impure 2-hydroxyethyl-2-buten-1-ol, which distilled over a wide range, was collected in the first receiver. This product was redistilled to give 111.5 g. of quite impure 2-hydroxyethyl-2-

buten-1-ol, b.p. 64–100° (0.5 mm.),  $n_D^{25}$  1.4610–1.4825. All this material was basic to litmus paper.

To 111.5-g. of the impure 2-hydroxyethyl-2-buten-1-ol contained in a 500-ml. flask was added 250 ml. of acetic anhydride and spontaneous, exothermic acetylation took place. After the solution was allowed to cool to room temperature, the acetic acid and the excess acetic anhydride were removed *in vacuo*. Finally the residue was distilled to yield 134.5 g. (50% over-all yield for the three steps from the aminodiol) of 2-acetoxyethyl-2-buten-1-yl acetate (VIII) containing some of the isomeric 2-methylene-1,3-butanediol diacetate, b.p. 80° (0.7 mm.),  $n_D^{25}$  1.4413–1.4431.

*Anal.* Calcd. for  $C_9H_{17}O_4$ : C, 58.05; H, 7.58. Found: C, 57.90; H, 7.81.

Vapor phase chromatography of this product at 207° in an instrument constructed in these laboratories<sup>12</sup> with a column made by the absorption of Dow Corning silicone grease on Chromosorb to the extent of 15% by weight indicated that this sample was 85 to 90% 2-acetoxyethyl-2-buten-1-ol acetate (VIII) (by comparison of the reaction time with that of an authentic sample run under the same conditions) and 10 to 15% the second component (by ratio of peak areas).

**Reaction of 2-(*N,N*-Dimethylamino)-2-ethyl-1,3-propanediol Diacetate with Hydrogen Peroxide.**—To 37.3 g. (0.161 mole) of 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol diacetate (VII) in a 100-ml. flask submerged in an ice bath was added 45 ml. of 30% hydrogen peroxide. After the spontaneous reaction had subsided, the mixture was allowed to stand for a day at room temperature. After this time, the excess hydrogen peroxide was decomposed catalytically at 50° in the presence of a platinumized platinum wire for 1 day. An aliquot of this amine oxide solution was added to an ethanol solution of picric acid. When the mixture was cooled, a picrate separated. It was removed by filtration and dried to yield a yellow solid, presumably the picrate of 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol *N*-oxide, m.p. 151–158° (dec.).

*Anal.* Calcd. for  $C_{13}H_{23}N_4O_{10}$ : C, 39.79; H, 5.14. Found: C, 40.07; H, 5.13.

**2-Acetoxyethyl-1,3-butadiene (II).**—The optimum temperature for the synthesis of 2-acetoxyethyl-1,3-butadiene (II) by the pyrolysis of 2-acetoxyethyl-2-buten-1-yl acetate (VIII) at a drop rate of 1 ml. per minute was determined by vapor phase chromatography by use of isobutylmethylcarbinyl acetate as an internal standard. Ternary solutions of known concentrations of isobutylmethylcarbinyl acetate, acetic acid, and 2-acetoxyethyl-1,3-butadiene (II) were chromatographed and the peak-area ratio for the diene compared to the standard for each solution was recorded. The gas chromatograph was a Perkin-Elmer Model 154, column 'A' at 131°; helium pressure, 20 p.s.i.; recorder voltage, 4 volts; and recorder range, 4. The optimum temperature was found to be 495°, with which a 46% conversion was indicated.

#### EFFECT OF TEMPERATURE ON THE PYROLYSIS OF 2-ACETOXYETHYL-2-BUTEN-1-YL ACETATE (VIII)

Temp., °C.	Starting material, g.	Standard, g.	Area ratio	Wt. ratio	Diene, g.	Yield, %
485	2.46	0.34	0.71	0.545	0.62	37
495	2.51	0.39	0.63	0.495	0.79	46
500–505	2.63	0.40	0.73	0.56	0.71	40
520–530	4.93	0.36	1.25	0.89	0.40	12
545–550	2.54	0.10	3.00	...	...	0

At a rate of 1 ml. per min., 76 g. (0.408 mole) of 2-acetoxyethyl-2-buten-1-yl acetate (VIII) was dropped through the pyrolysis apparatus previously described<sup>13</sup> at 495°. The

(12) W. J. Bailey and W. H. Hale, *J. Am. Chem. Soc.*, **81**, 647 (1959).

(13) W. J. Bailey and C. King, *ibid.*, **77**, 75 (1955).

(11) A. Byers and W. J. Hickinbottom, *J. Chem. Soc.*, 284 (1948).

pyrolysate was condensed in a spiral, water-cooled condenser and collected in a flask immersed in an acetone-Dry Ice bath; however, some uncondensed gaseous materials passed through this trap. The products were dissolved in 200 ml. of ether and the resulting solution was washed with four 25-ml. portions of water. The water washings were made basic to phenolphthalein with sodium hydroxide solution and were extracted with two 25-ml. portions of ether. After the combined ether solutions were dried over anhydrous magnesium sulfate, the ether was removed at atmospheric pressure and the product was fractionated at reduced pressure through a 10-in. Vigreux column, to yield 17.4 g. (34%) of 2-acetoxymethyl-1,3-butadiene (II), b.p. 55–60° (30 mm.),  $n_D^{20}$  1.4525, and 25 g. of a high-boiling residue, presumably a mixture of 2-acetoxymethyl-2-buten-1-yl acetate (VIII) and 2-methylene-1,3-butanediol diacetate. The yield of 2-acetoxymethyl-1,3-butadiene (II), based on unrecovered diacetates, was 51%.

**Bis(2-butadienylmethyl) Acetal (IX).**—By the procedure of Croxall, Glavis, and Neber,<sup>7</sup> 10.3 g. (0.123 mole) of 2-hydroxymethyl-1,3-butadiene in a 50-ml. flask fitted with a reflux condenser through which nitrogen was continuously passed were added 5.25 g. (0.016 mole) of vinyl acetate, a small amount of *N*-phenyl- $\beta$ -naphthylamine, and 0.1 g. of red mercuric oxide. With the addition of 0.25 ml. of boron trifluoride etherate, spontaneous warming took place. After the mixture was allowed to stand for 10 min. and the reactants had begun to cool, the solution was poured into 100 ml. of a saturated sodium carbonate solution in a separatory funnel. An oil which separated on extraction was then dissolved in 20 ml. of ether and the ether solution was dried over anhydrous potassium carbonate. The solution was distilled, first at atmospheric pressure to remove the ether and then at reduced pressure through a 6-in. Vigreux column to yield 3.1 g. (30%) of recovered 2-hydroxymethyl-1,3-butadiene; 2.6 g. (23%) of bis(2-butadienylmethyl) acetal (IX), b.p. 65° (1.0 mm.),  $n_D^{20}$  1.4802; and 0.65 g. of an insoluble polymeric residue. The yield, based on unrecovered 2-hydroxymethyl-1,3-butadiene, was 31%.

*Anal.* Calcd. for  $C_{12}H_{18}O_2$ : C, 74.18; H, 9.34. Found: C, 74.19; H, 9.38.

An infrared spectrum of this acetal run in carbon tetrachloride solution gave sharp peaks at 906 and 990  $cm^{-1}$  (associated with out-of-plane deformations of the vinyl group), a sharp peak at 1600  $cm^{-1}$  (assigned to conjugated carbon-to-carbon double bond stretching), and a doublet at 1100 and 1137  $cm^{-1}$  (assigned to the C—O—C—O—C structure in the acetal on the basis of similar bands previously found in other acetals<sup>14</sup>). The fact that no peak was observed in the 3100–3600- $cm^{-1}$  region indicated that there was little or no starting alcohol I present in this sample. Vapor-phase chromatography at 205° on a silicone grease-on-Chromosorb column gave only one peak.

**Bis(2-butadienylmethyl) Hexamethylenedicarbamate (X).**—To 3.09 g. (0.037 mole) of 2-hydroxymethyl-1,3-butadiene (I) was added 1.62 g. (0.0097 mole) of hexamethylene diisocyanate in which 0.01 g. of *N*-phenyl- $\beta$ -naphthylamine

had been dissolved. After the mixture had been allowed to stand overnight at room temperature, no crystallization had occurred, but after it was cooled for a few minutes at  $-20^\circ$ , the solution solidified to a white mass. The solid was dissolved in 15 ml. of methylene chloride and recrystallized by the addition of 200 ml. of 60–80° petroleum ether, followed by cooling of the resulting solution at  $-20^\circ$  for 2 hr. The product was collected on a filter and air-dried to yield 2.45 g. (76%) of bis(2-butadienylmethyl) hexamethylenedicarbamate (X), softening at 79–80°. This compound did not liquefy completely but remained semisolid at 200°.

*Anal.* Calcd. for  $C_{18}H_{28}N_2O_4$ : C, 64.26; H, 8.38. Found: C, 64.19; H, 8.38.

This sample was soluble in dimethylformamide, acetone, methylene chloride, and benzene and somewhat soluble in 60–80° petroleum ether. The infrared spectrum, run on a Nujol mull, gave sharp peaks at 897, 908, 987, and 1595  $cm^{-1}$  associated with the methylene group, vinyl group (two bands), and the conjugated double bond, respectively.<sup>10</sup> Strong bands were also observed at 1693, 1538, and 3370  $cm^{-1}$  assigned to the "Amide I," "Amide II," and N—H stretching frequencies.

After being allowed to stand for 5 days at room temperature, the solid bifunctional diene became insoluble in benzene, methylene chloride, and dimethylformamide, although its external appearance had not changed. The infrared spectrum, again on a Nujol mull, had changed markedly. The bands at 1693, 1538, and 3370  $cm^{-1}$  remained strong, while the bands at 897, 908, 987, and 1595  $cm^{-1}$  became very weak. After about 2 weeks the material began to yellow, but if the diurethane was stored at  $-20^\circ$ , it retained its original properties for several weeks.

**Bis(2-butadienylmethyl) *m*-Xylylenedicarbamate (XII).**—To 0.65 g. (0.0077 mole) of 2-hydroxymethyl-1,3-butadiene (I) were added 0.50 g. (0.0026 mole) of *m*-xylylene diisocyanate, a small amount of *N*-phenyl- $\beta$ -naphthylamine, and 0.01 g. of triethylenediamine. After the solution was warmed slightly for 10 min., crystallization of a colorless adduct commenced. When solidification appeared complete, the mixture was dissolved in 5 ml. of methylene chloride. The resulting solution was allowed to stand at room temperature for 1 hr. and was then poured into 100 ml. of petroleum ether (b.p. 60–80°). After this solution was cooled to  $-20^\circ$ , the precipitate was removed by filtration and air dried to yield 0.70 g. of bis(2-butadienylmethyl) *m*-xylylenedicarbamate. By evaporation of some of the solvent, followed by additional cooling, another 0.14 g. of the urethane was obtained for a total of 0.84 g. (91%) of bis(2-butadienylmethyl) *m*-xylylene carbamate (XII), which did not melt completely on heating, presumably because of thermal polymerization.

*Anal.* Calcd. for  $C_{20}H_{24}N_2O_4$ : C, 67.39; H, 6.74. Found: C, 67.53; H, 6.86.

The infrared spectrum, run on a Nujol mull, gave peaks at 3340, 1700, and 1550  $cm^{-1}$  attributed to N—H stretching, and the "Amide I" and "Amide II" frequencies, respectively.<sup>14</sup> Also prominent were bands at 1600, 990, and 910  $cm^{-1}$  for conjugated double bond and vinyl group characteristic frequencies. A strong band observed at 785  $cm^{-1}$  is significant in that this is the region for absorption due to C—H out-of-plane bending when three adjacent hydrogen atoms occur on an aryl ring (*m*-disubstituted benzenes).<sup>14</sup>

(14) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 34 and 119.