Aminobutadienes. IX.[1] The Synthesis of 2-Phthalimidomethyl-1, 3-butadiene

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In previous papers of this series, we reported that 1-phthalimido-,[2] 1-succinimido-,[2] and 1-(2-oxopyrrolidino)-1, 3-butadienes[1] were synthesized from 1, 3-butadiene, and that 2-phthalimido- and 2-succinimido-1, 3-butadienes[3] were derived either from ethyl α-oxyiminoacetoacetate or D-threonine. Among these monomers, 1-phthalimido- and 1-succinimido-1, 3-butadienes are easily polymerized in the presence of either radical[4] or cationic initiators,[5] while 2-phthalimido-1, 3-butadiene is very easily polymerized by radical initiators,[6] but not cationic ones.[6] The monomer reactivity ratios and Alfrey-Price *Q-e* values were determined by copolymerizations with styrene.[6,7]

In this paper, we wish to report on the synthesis of 2-phthalimidomethyl-1, 3-butadiene (VII) from isoprene.

The addition reaction of hypochlorous acid to isoprene was carried out by passing carbon dioxide gas into a liquid of isoprene and bleaching powder dispersed in a large amount of water. The main product was a fraction with a boiling point of 52—54°C/27 mmHg. The elemental analysis and infrared spectrum showed that this product was 1-chloro-2-methyl-3-buten-2-ol (I), and not either the 1, 4-, 3, 4-, or 1, 2, 3, 4-addition product. From the remaining part, white crystals melting at 81.5—83°C were separated. These crystals were found by elemental analysis to be isoprene dichlorohydrine. The infrared spectrum of this dichlorohydrine reveals the bands of primary and tertiary alcohols. On the other hand, this dichlorohydrine does not have the α, β-glycol unit in its structure, because it is negative on periodic acid oxidation, and its melting point does not agree with that of 1, 4-dichloro-2-methyl-2, 3-butandiol (mp 106.5°C).[8] Therefore, this dichlorohydrine was confirmed to be 1, 3-dichloro-2-methyl-2, 4-butandiol (II).

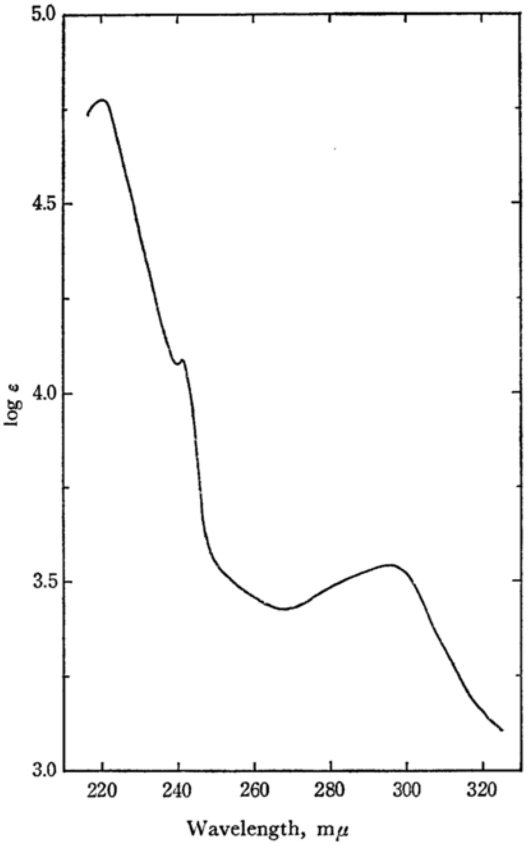

Fig. 1. Ultraviolet absorption spectrum of 2-phthalimidomethyl-1, 3-butadiene (VII) in ethanol. λ_{max} 219.5 mμ (ε 6.23×10^4); 240.5 mμ (1.28×10^4); 294 mμ (3.56×10^3).

The dehydrochlorination of I by using alkali was easily carried out to give 1, 2-epoxy-2-methyl-3-butene (III), bp 80—82°C. III can also be obtained by the reaction of isoprene with perbenzoic acid.[9]

1-Amino-2-methyl-3-buten-2-ol (IV) was then prepared by the ammonolysis of III, according to the method of Ettlinger.[10]

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1) Paper VIII: K. Murata and A. Terada, This Bulletin, **40**, 414 (1967).

2) A. Terada and K. Murata, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 490 (1962).

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5) K. Murata and A. Terada, *Makromol. Chem.*, **109**, 260 (1967).

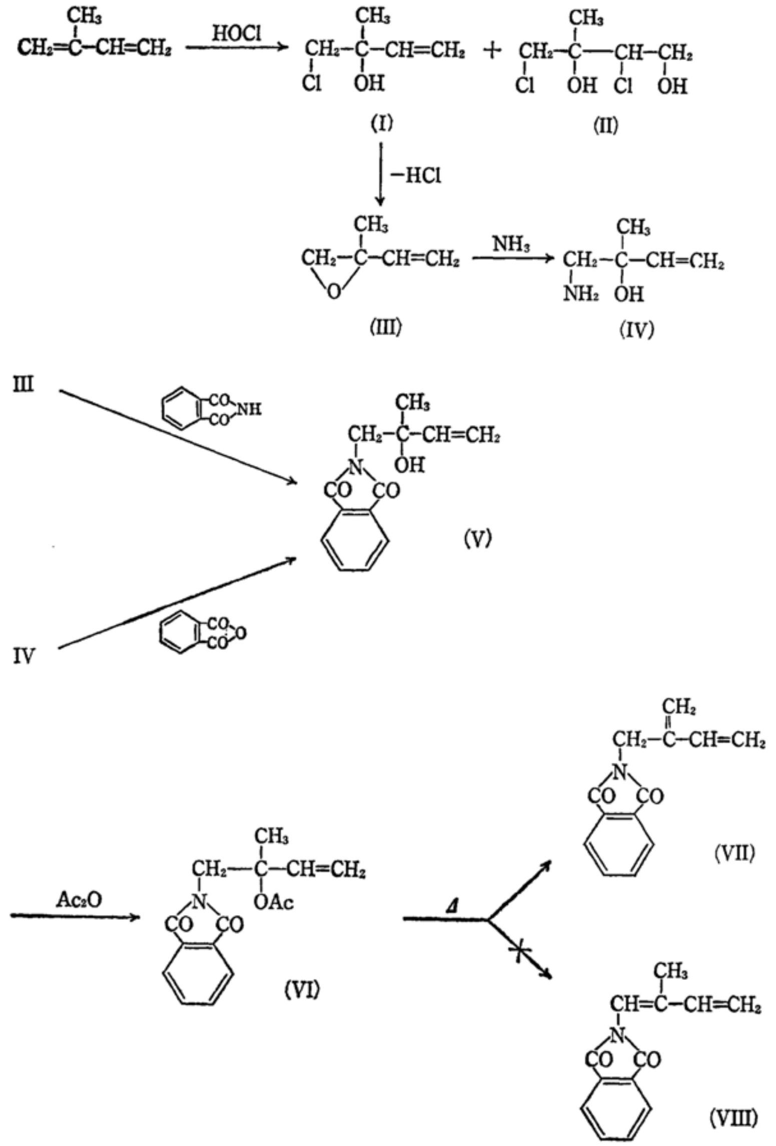
6) K. Murata and A. Terada, *J. Polymer Sci., A-1*, **4**, 2989 (1966).

7) K. Murata and A. Terada, This Bulletin, **39**, 2494 (1966).

8) W. J. Jones and H. G. Williams, *J. Chem. Soc.*, **1934**, 835.

9) R. Pummerer and W. Reindel, *Ber.*, **66**, 335 (1933).

10) M. G. Ettlinger, *J. Am. Chem. Soc.*, **72**, 4792 (1950).



Scheme 1. The synthetic route of 2-phthalimidomethyl-1, 3-butadiene.

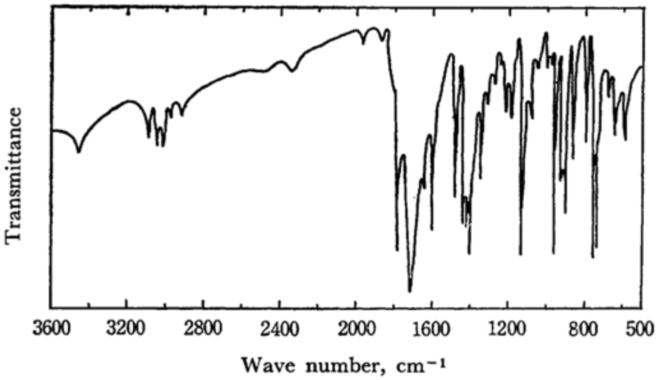


Fig. 2. Infrared absorption spectrum of 2-phthalimidomethyl-1, 3-butadiene (VII) in KBr disk.

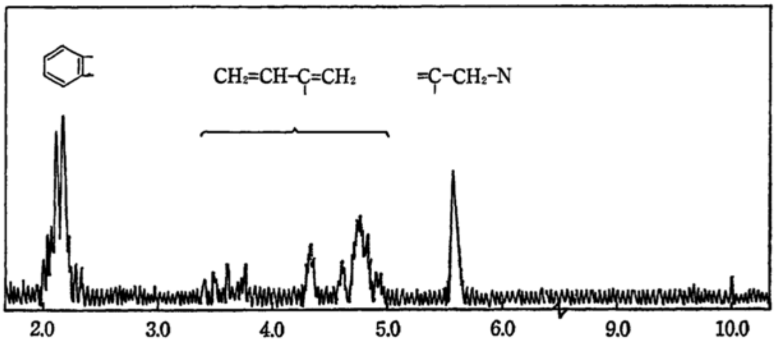


Fig. 3. NMR spectrum of 2-phthalimidomethyl-1, 3-butadiene (VII) in carbon tetrachloride at 60 Mc.

2-Methyl-1-phthalimido-3-buten-2-ol (V), mp 102—103°C, was obtained in a theoretical yield by the condensation reaction of IV with phthalic anhydride at 200°C. Although this intermediate, V, could also be prepared by the direct addition of phthalimide to III at 150°C using an alkali catalyst, the yield was very poor due to the difficult solubility of phthalimide in III.

The acetylation of V was carried out according to the ordinary method to give 2-acetoxy-2-methyl-1-phthalimido-3-butene (VI), mp 71—72°C.

The pyrolysis of VI at 550°C gave colorless crystals with a melting point of 114.5—116°C. The ultraviolet absorption spectrum is shown in Fig. 1, in which a strong absorption maximum appears at 219.5 mμ, almost the same position as those of isoprene (220 mμ),11) 2-phthalimido-1, 3-butadiene (219 mμ),3) and 2-succinimido-1, 3-butadiene (219.5 mμ),3) all of which have been characterized as 2-substituted-1, 3-butadienes. On the other hand, 1-substituted-1, 3-butadienes, such as 1-phthalimido-1, 3-butadiene, 1-succinimido-1, 3-butadiene, and 1-(2-oxopyrrolidino)-1, 3-butadiene, show different absorption maxima, at 278.5,2) 248,2) and 268.5 mμ1) respectively. The infrared absorption spectrum reveals a conjugated diene band at 1600 cm^{-1}, shown in Fig. 2, and the NMR spectrum in Fig. 3 shows methylene protons at 5.57 ppm, but no methyl protons.

The crystalline product prepared by the deacetylation of VI should be either 2-phthalimidomethyl-1, 3-butadiene (VII) or 2-methyl-1-phthalimido-1, 3-butadiene (VIII); from the results of the ultraviolet and NMR spectra, it is concluded that the product is VII.

Finally, a Diels-Alder reaction of VII with maleic anhydride gave 4-phthalimidomethyl-1, 2, 3, 6-tetrahydrophthalic anhydride.

Experimental

The infrared spectra were measured with a Perkin-Elmer spectrophotometer, model 221, and a Hitachi infrared spectrophotometer, model EPI-S. The NMR and ultraviolet spectra were recorded with a Varian NMR spectrometer, model A-60, and a Hitachi recording spectrophotometer, model EPS-2, respectively.

The Addition of Isoprene with Hypochlorous Acid. Into a dispersed solution of 50 g of isoprene, 100 g of bleaching powder (available chlorine 60%) and 1.0 g of Nonion N-1000 (Nissan Oils and Fats Co., Ltd.) in 1.2 *l* of water, 40 *l* of carbon dioxide gas was passed under stirring for 2 hr at 0—5°C. The reaction mixture was filtered to remove calcium carbonate, and then saturated with sodium chloride and extracted four times with ether. The combined ether extract was dried over calcium chloride. Then, after the ether had been removed, the residue was distilled through a Widmer column (length 200 mm) under a vacuum; 33.3 g (37.6%) of 1-chloro-2-methyl-3-buten-2-ol (I) was thus obtained as a colorless liquid with a boiling point of 52—54°C/27 mmHg.

Found: C, 49.66; H, 7.69%. Calcd for C_5H_9OCl (I): C, 49.81; H, 7.52%.

IR: 3470 (OH); 1175 (tertiary alcohol); 1870, 1410, 1290, 990, 927 (vinyl); 752 cm^{-1} (C–Cl).

After the I had been distilled out, the liquid residue was allowed to stand for a long time at room temperature; then a small amount of crystals was separated. When those crude crystals were recrystallized from benzene, isoprene dichlorohydrine was obtained as white crystals with a melting point of 81.5—83°C. This dichlorohydrine did not react with periodic acid.12)

Found: C, 34.55, 34.80; H, 5.90, 6.02%. Calcd for $C_5H_{10}O_2Cl_2$ (II): C, 34.70; H, 5.78%.

IR: 3330 (OH); 1175 (tertiary alcohol); 1280, 1075 (primary alcohol); 724 cm^{-1} (C–Cl).

The Dehydrochlorination of I. To 200 g of 50% aqueous sodium hydroxide, 85.0 g of I was added, drop by drop, with a thorough agitation at about 130°C over a 3.0 hr period. In the course of this reaction, the reaction product was distilled with water; the distillate was separated into two phases, in both of which sodium chloride was then saturated. The upper organic layer was separated, dried over calcium chloride,

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11) H. Brooker, L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, **1940**, 1453.

12) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y. (1956), p. 129.

and distilled to yield 43.0 g (72.4%) of 1,2-epoxy-2-methyl-3-butene (III), bp 80—82°C. Lit., bp 81°C/735 mmHg.[9]

IR: 1860, 1425, 1300, 988, 915 (vinyl); 1233, 883 cm^{-1} (epoxide.)

The Ammonolysis of III. Into 500 g of ammonia water (concentration 28%), 36.3 g of III was added, drop by drop, under stirring at 5—10°C. After the addition had been finished, the mixture was stirred for 48 hr at room temperature. The excess ammonia water was removed through a Widmer column under a vacuum, and finally 20.6 g (47.1%) of 1-amino-2-methyl-3-buten-2-ol (IV) was distilled out at 50—54°C/4.5—6 mmHg.

IR: 3500 (OH); 3420—3300, 1618 (primary amine); 1170 (tertiary alcohol); 1870, 1655, 1427, 1305, 1000, 925 cm^{-1} (vinyl).

The Condensation of IV with Phthalic Anhydride. A mixture of 6.0 g of IV and 8.8 g of phthalic anhydride was slowly heated to 200°C, and then kept for half an hour at this temperature in order to remove 1.0 m*l* of water. The crude product (14.0 g) crystallized when it came to room temperature. Recrystallization from water gave 2-methyl-1-phthalimido-3-buten-2-ol (V) as colorless needles with a melting point of 102—103°C.

Found: C, 67.50, 67.67; H, 5.80, 5.83; N, 6.05%. Calcd for $C_{13}H_{13}O_3N$ (V): C, 67.52,; H, 5.67; N, 6.06%.

IR: 3520 (OH): 1770, 1705 (C=O, phthalimido); 1610 (phenyl); 1180 (tertiary alcohol); 1867, 1655, 1411, 1300, 998, 928 (vinyl); 725, 712 cm^{-1} (*o*-disubstituted benzene).

The Addition of Phthalimide to III. A mixture of 8.4 g of III and 14.7 g of phthalimide, plus 5 drops of 30% aqueous potassium hydroxide as a catalyst, was heated in a sealed tube for 24 hr at 150°C. After standing for one day, the reaction product was extracted with benzene; a solid residue (8.7 g) remained. The recrystallization of this residue from water gave colorless needles with a melting point of 230—233°C. These crystals were confirmed to be phthalimide by a mixed-melting-point test with an authentic sample.

After the benzene had been removed from the extract, the oily residue was subjected to distillation under a vacuum; it thus gave a fraction with a boiling point of 163—165°C/3 mmHg, 6.3 g (27%). This fraction slowly crystallized on standing. Recrystallization from water gave colorless needles, mp 102—105°C. These crystals were confirmed to be V by a mixed-melting-point test.

The Acetylation of V. To 4.0 g of V, 25 m*l* of acetic anhydride and 0.5 g of anhydrous sodium acetate as a catalyst were added; the mixture was then refluxed for 10 hr. After the excess acetic anhydride had been removed under a vacuum, the oily residue was poured into a large amount of cold water and neutralized with sodium bicarbonate. Then crude crystals appeared; they were dried after washing with water. Recrystallization from benzene-petroleum benzine gave 2-acetoxy-2-methyl-1-phthalimido-3-butene (VI) as colorless crystals, mp 71—72°C.

Found: C, 65.92, 66.01; H, 5.65, 5.71; N, 5.10%. Calcd for $C_{15}H_{15}O_4N$ (VI): C, 65.92; H, 5.53; N, 5.13%.

IR: 1770, 1725 (C=O, phthalimido); 1750 (C=O, ester); 1235 (acetate); 1610 (phenyl); 1650, 1395, 1300, 980, 940 (vinyl); 725, 710 cm^{-1} (*o*-disubstituted benzene).

The Pyrolysis of VI. A solution of 20.0 g of VI in 60 m*l* of acetone was pyrolyzed under a nitrogen atmosphere by being dropped into a reaction tube of porcelain (ϕ 20 mm, length 500 mm) kept at 550°C[13] in an electric furnace (ϕ 30 mm, length 230 mm). The dropping time needed was 2.3 hr. The pyrolyzate was then poured into cold water, neutralized with sodium bicarbonate, and extracted with benzene. The extract was dried over anhydrous sodium sulfate. After the benzene had been removed under a vacuum, the remaining part crystallized. By extraction with hot petroleum benzine and letting the mixture stand in a refrigerator, crude crystals (4.5 g) of mp 92—109°C were obtained; they were then recrystallized from petroelum benzine to give 2-phthalimidomethyl-1, 3-butadiene (VII) as colorless crystals, mp 114.5—116°C. The ultraviolet and NMR spectra are shown in Figs. 1 and 3 respectively.

Found: C, 73.23; H, 5.25; N, 6.44%. Calcd for $C_{13}H_{11}O_2N$ (VII): C, 73.22; H, 5.20; N, 6.57%.

IR (Fig. 2): 1770, 1700 (C=O, phthalimido); 1870, 1400, 1305, 958, 912 (vinyl); 1615 (phenyl); 1600 (conjugated diene); 725, 710 cm^{-1} (*o*-disubstituted benzene).

The Diels-Alder Reaction of VII with Maleic Anhydride. A solution of 0.27 g of VII and 0.14 g of maleic anhydride in 10 m*l* of benzene was refluxed on a water bath for 2 hr. After the benzene had been removed, the residue was crystallized by letting it stand overnight. Recrystallization from benzene-petroleum benzine gave 4-phthalimidomethyl-1, 2, 3, 6-tetrahydrophthalic anhydride as white crystals, mp 146—147.5°C.

Found: C, 65.73, 65.78; H, 4.25, 4.45; N, 4.36, 4.33%. Calcd for $C_{17}H_{13}O_5N$: C, 65.59; H, 4.21; N, 4.50%.

IR: 1850 (C=O, five-membered cyclic anhydride); 1770, 1720 (C=O, phthalimido); 1610 (phenyl); 721, 710 cm^{-1} (*o*-disubstituted benzene).

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[13] This temperature was measured in the central part of the tube by a thermo-couple.