# Aminobutadienes. VIII. The Synthesis of 1-(2-Oxopyrrolidino)-1, 3-butadiene[1]

Kenichi MURATA and Akira TERADA*1

*Government Industrial Research Institute, Osaka, Midorigaoka, Ikeda, Osaka*

(Received June 24, 1966)

It has previously been reported that 1-phthalimido- and 1-succinimido-1, 3-butadienes were synthesized from 1, 3-butadiene[2] and polymerized easily in the presence of radical[3] and cationic initiators.[4] In this paper, we wish to report the preparation of 1-(2-oxopyrrolidino)-1, 3-butadiene (III) which differs from 1-succinimido-1, 3-butadiene by just the replacement of one methylene group with a carbonyl group.

The reaction of 1-amino-3-buten-2-ol with $\gamma$-butyrolactone afforded 1-(2-oxopyrrolidino)-3-buten-2-ol (I) in a 59% yield. Although this intermediate (I) could also be prepared by the condensation of 1-chloro-3-buten-2-ol with sodium $\alpha$-pyrrolidone, the yield was far lower than that of the first method in spite of the quantitative formation of sodium chloride. The reason of this low yield is that the dehydrochlorination of 1-chloro-3-buten-2-ol by sodium $\alpha$-pyrrolidone is preferable to the condensation reaction. The I intermediate was also made in a 65% yield by the addition reaction of $\alpha$-pyrrolidone to 1, 2-epoxy-3-butene in the presence of alkali, according to the method previously reported in the

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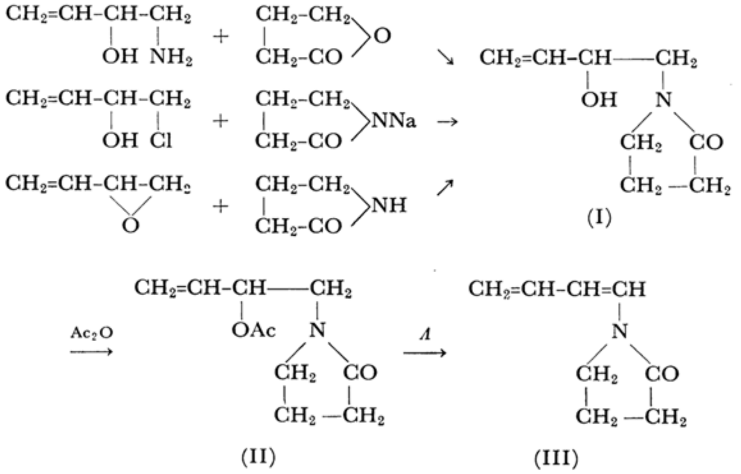
*1 Present address: Department of Industrial Chemistry, Kyushu Institute of Technology, Tobata-ku, Kita-Kyushu.

[1] Presented by K. Murata at the Tokai Meeting of the Chemical Society of Japan, Nagoya, November, 1963.

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

[3] Presented by A. Terada and K. Murata at the Tokuyama Meeting of the Chemical Society of Japan, Tokuyama, May, 1961.

[4] Presented by A. Terada and K. Murata at the Autumn joint Meeting of Chemistry-related Societies, Tokyo, October, 1962.



syntheses of 1-phthalimido- and 1-succinimido-3-buten-2-ols.[2] 1-(2-oxopyrrolidino)-2-acetoxy-3-butene (II) was then obtained from I by acetylation with acetic anhydride.

The pyrolysis of II at 550°C gave the final product (III) as colorless plates with a melting point of 59.5—61°C. As may be seen in Fig. 1, a comparison of the ultraviolet absorption spectra of III and *N*-vinyl pyrrolidone indicates that the absorption maximum for III shifted to a longer wavelength and that its intensity was stronger than that of *N*-vinyl pyrrolidone. On the other hand, the infrared spectrum revealed a conjugated diene band at 1602 cm$^{-1}$. A Diels-Alder reaction of III with maleic anhydride gave 3-(2-oxopyrrolidino)-1, 2, 3, 6-tetrahydrophthalic anhydride.

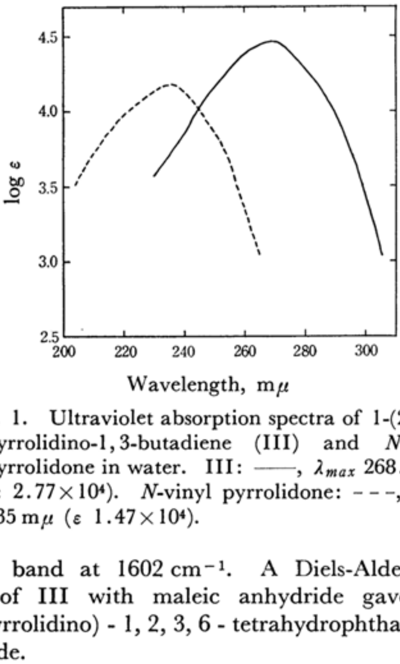


Fig. 1. Ultraviolet absorption spectra of 1-(2-oxopyrrolidino-1, 3-butadiene (III) and *N*-vinyl pyrrolidone in water. III: ——, $\lambda_{max}$ 268.5 mμ ($\varepsilon$ 2.77×10$^4$). *N*-vinyl pyrrolidone: - - -, $\lambda_{max}$ 235 mμ ($\varepsilon$ 1.47×10$^4$).

The polymerization and copolymerization of this monomer (III) will be reported in detail elsewhere.

## Experimental

**The Reaction of 1-Amino-3-buten-2-ol with γ-Butyrolactone.** To 9.3 g of 1-amino-3-buten-2-ol[5] 9.3 g of γ-butyrolactone was added, and the mixture was heated at 180°C in a sealed glass tube for 24 hr. By distilling the product, 1-(2-oxopyrrolidino)-3-buten-2-ol (I) was obtained as a fraction with a boiling point of 120—123°C/0.4 mmHg; 9.0 g (59%), $n_D^{21}$ 1.4961.

Found: C, 62.10, 62.03; H, 8.50, 8.57; N, 9.71%. Calcd for $C_8H_{13}O_2N$ (I): C, 61.91; H, 8.44; N, 9.03%.

IR: 3380, 1138 (OH); 1850, 1427, 1293, 997, 928 (vinyl); 1665 cm$^{-1}$ (C=O).

**The Condensation of 1-Chloro-3-buten-2-ol with Sodium α-Pyrrolidone.** A mixture of 9.0 g of 1-chloro-3-buten-2-ol[6] and 9.0 g of sodium α-pyrrolidone[7] was heated at 150—160°C for 6 hr. The filtration of the reaction mixture gave a quantitative yield of sodium chloride. From the filtrate, three fractions were obtained by distillation: A) bp 70—97°C/3.5 mmHg, 3.2 g, B) bp 98—131°C/3.5 mmHg, 2.4 g and C) bp 132—135°C/3.5 mmHg, 2.7 g. A) was known from its infrared spectrum to be crude α-pyrrolidone. The infrared spectrum and the refractive index ($n_D^{21}$ 1.4960) of C) were essentially identical with those of I, B) was a middle fraction.

**The Reaction of α-Pyrrolidone and 1, 2-Epoxy-3-butene.** To 15.0 g of 1, 2-epoxy-3-butene,[6] there were added 18.2 g of α-pyrrolidone and 5 drops of 30% aqueous potassium hydroxide; the mixture was then heated in a sealed tube at 150°C for 24 hr. The following fractions were obtained by distilling the product: D) bp 50—114°C/0.4 mmHg, 6.7 g and E) bp 122—125°C/0.4 mmHg, 21.6 g. The main component of D) was α-pyrrolidone (infrared spectrum); its infrared spectrum and refractive index ($n_D^{21}$ 1.4956) of E) both agreed closely with those of I.

Different methods for the preparation of I were also investigated; the results are shown in Table 1.

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

6) R. G. Kadesch, *ibid.*, **68**, 41 (1946).

7) U. S. Pat. 2727017 (1955).

Table 1. The addition reaction of $\alpha$-pyrrolidone to 1,2-epoxy-3-butene

| Catalyst | Temperature °C | Time hr | Yield % |
|---|---|---|---|
| None | 180 | 24 | 0 |
| None | 150 | 45 | 16 |
| $C_2H_5ONa$ | 150 | 24 | 36 |
| 30% NaOH aq. | 150 | 24 | 63 |
| 30% KOH aq. | 150 | 24 | 65 |

**The Acetylation of I.** A mixture of 14.0 g of I, 1.0 g of anhydrous sodium acetate, and 30 m*l* of acetic anhydride was heated for 20 hr in a boiling water bath. Excess acetic anhydride was distilled, and the oily residue was poured into cold water, neutralized with sodium bicarbonate, and then extracted with benzene. The benzene layer was separated and dried over anhydrous sodium sulfate. After the benzene had then been removed, the residue was distilled to obtain 10.3 g of 1-(2-oxopyrrolidino)-2-acetoxy-3-butene (II); bp 119—122°C/3.5 mmHg, $n_D^{21}$ 1.4730.

Found: C, 61.19, 61.15; H, 7.80, 7.71; N, 7.02%. Calcd for $C_{10}H_{15}O_3N$ (II): C, 60.89; H, 7.67; N. 7.10%.

IR: 1850, 1427, 1292, 988, 928 (vinyl); 1690 (C=O, $\alpha$-pyrrolidone); 1745, 1240, 1020 $cm^{-1}$ (acetate).

**The Pyrolysis of II.** A solution of 10.0 g of II in 35 m*l* of acetone was added, drop by drop, over a 1.5 hr period, to a reaction tube of porcelain ($\phi$ 20 mm, length 500 mm) heated at 550°C[8] in an electric furnace ($\phi$ 30 mm, length 230 mm) under a nitrogen atmosphere. The pyrolyzate was poured into cold water, neutralized with sodium bicarbonate, and extracted with benzene. The extract was dried over anhydrous sodium sulfate, the benzene was removed, and the residue was distilled. The fraction (2.0 g) with a boiling point of 94—104°C/4 mmHg crystallized immediately. Recrystallization from petroleum benzine yielded 1-(2-oxopyrrolidino)-1, 3-butadiene (III) as colorless plates, mp 59.5—61°C.

Found: C, 70.13, 70.06; H, 8.27, 8.16; N, 10.16%. Calcd for $C_8H_{11}ON$ (III): C, 70.04; H, 8.08; N, 10.21%.

IR: 1850, 1428, 1300, 995, 932 (vinyl); 1638 (C=C); 1602 (conjugated diene); 1683 $cm^{-1}$ (C=O).

The ultraviolet spectrum is shown in Fig. 1.

**The Reaction of III with Maleic Anhydride.** A solution of 0.39 g of III and 0.28 g of maleic anhydride in 5 m*l* of benzene was refluxed on a water bath for 2 hr. After the benzene had been removed, the residue was crystallized by adding petroleum benzine. The crude crystals were recrystallized from benzene - petroleum benzine to give 0.5 g of 3-(2-oxopyrrolidino)-1, 2, 3, 6-tetrahydrophthalic anhydride, mp 122—124°C.

Found: C, 61.10; H, 5.99; N, 5.94%. Calcd for $C_{12}H_{13}O_4N$: C, 61.27; H, 5.57; N, 5.96%.

IR: 1840, 1765 (C=O, five-membered cyclic anhydride); 1670 $cm^{-1}$ (C=O, $\alpha$-pyrrolidone).

The authors wish to thank Professor Shizunobu Hashimoto of Doshisha University and Dr. Isao Shiihara of this Institute for their helpful suggestions during this work.

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