## BRIEF COMMUNICATIONS

# INTRAMOLECULAR CYCLIZATION OF VINYLACETYLENIC SYSTEMS

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As was shown earlier [1], the formation of cyclic products of the type of (I) in the condensation of cis-1bromo-2,3-dimethylpentene-2-yne-4 with maleic or acetoacetic esters proceeds as a result of nucleophilic intramolecular addition, due to the approach of the reaction centers in the intermediate cis-vinylacetylenic system



For a further investigation of this interesting case of the Michael addition, previously known only for activated acetylenic bonds [2], we studied the condensation of cis-1-chloropentene-2-yne-4 (II) with malonic ester. It was found that in the presence of sodium alcoholate at  $20-25^{\circ}$ , this reaction gives a mixture of two products in a 3:2 ratio according to the data of gas-liquid chromatography. When the reaction mass is further heated (2 h at  $70^{\circ}$ ), the amount of one of the products, corresponding to the second peak on the chromatogram, is sharply reduced to 4-6%. After distillation and subsequent treatment of the mixture obtained with an alcohol solution of silver nitrate, an individual product was isolated, which does not contain a terminal acetylenic group, corresponds to the first peak on the gas-liquid chromatogram, and according to the data of the UV and IR spectra, possesses the structure of the diethyl ester of 2-methylenecyclopentene-3-dicarboxylic-1,1 acid (IV)



The structure of this product was demonstrated by saponification to the monoester (V) and the dicarboxylic acid (VI), decarboxylation of which produced the dimer of 2-methylcyclopentadiene-1,3-carboxylic-1 acid (VII). In accord with these data, the second reaction product, which arises as an intermediate product in the formation of (IV), should have the structure of the diethyl ester of cis-hexene-3-yne-5-dicarboxylic-1,1 acid (III), since only its intramolecular cyclization will lead to the cyclic diester (IV). Thus, the reaction of nucleophilic intramolecular addition at the terminal acetylenic bond is sufficiently general for such cis-vinylacetylenic system, which contain a nucleophilic center in the homoallyl position. The previously noted formation of substituted pyrroles in the condensation of cis-2-chlorohexene-3-yne-5 with various amines [3] may serve as a supplementary confirmation of this conclusion. However, a necessary condition for the accomplishment of intramolecular cyclization, in addition to a

cis-configuration at the double bond and the presence of a nucleophilic center in the homoallyl position, is sufficient reactivity of the triple bond itself. We have established that in the condensation of the dibromide, obtained from decadiene-2,8 (dicis)-diyne-4,6-diol-1,10 (VIII) with sodium malonic ester, followed by saponification, only dodecadiene-3,9(dicis)-diyne-5-,7-tetracarboxylic-1,1,12,12 acid (IX), the structure of which was confirmed by the data of the UV and IR spectra, can be isolated, in a yield of up to 20%:

# $\begin{array}{c} \text{HOCH}_{2}\text{CH} = \text{CH}(\text{C} \equiv \text{C})_{2}\text{CH} = \text{CHCH}_{2}\text{OH} \xrightarrow{\text{1.PBr}_{3}} (\text{HO}_{2}\text{C})_{2}\text{CHCH}_{2}\text{CH} = \\ (\text{VIII}) \xrightarrow{\text{2.NaCH}(\text{CO}_{2}\text{Et})_{2}} (\text{HO}_{2}\text{C})_{2}\text{CHCH}_{2}\text{CH} = \\ = \text{CH}(\text{C} \equiv \text{C})_{2}\text{CH} = \text{CHCH}_{2}\text{CH}(\text{CO}_{2}\text{H})_{2} \end{array}$

Evidently in such a system, as a result of symmetrical displacement of the electron density, there is a decrease in the reactivity of the triple bond, as a result of which the reaction of intramolecular nucleophilic addition is hindered.

(IX)

### EXPERIMENTAL SECTION

Diethyl Ester of 2-Methylenecyclopentene-3-dicarboxylic-1,1 Acid (IV). To a solution of sodium malonic ester (from 0.1 gram atom of Na in 100 ml of alcohol), 10 g of the cis-chloride was added with vigorous mixing at 20-25° [4], and the mixture was exposed for one hour. An analysis of the composition of the mixture obtained by the method of gas-liquid chromatography (1% silicone elastomer on NaCl, 125°) gives two peaks with a ratio of approximately 3:2. The mixture was boiled for 2 h, and after the usual treatment and vacuum distillation, we obtained 15.4 g (yield 70%) of a liquid mixture of the diesters (III) and (IV), with b. p. 65-80° (0.07 mm). According to the data of gas-liquid chromatography, the content of (III) before and after distillation did not exceed 4-6% (a weak test with an ammonia solution of AgNO<sub>3</sub>); 5 g of the condensation product was shaken for 3 h at 20° with a solution of 10 g AgNO<sub>3</sub> in 200 ml of alcohol, the precipitate formed was filtered off, and after redistillation of the residue, 3.8 g of the cyclic diester (IV), corresponding to the first peak on the chromatogram, with b. p. 74-76° (0.07 mm); nD<sup>19-5</sup> 1.4750;  $\lambda_{max}$  (in alcohol) 230 mµ  $\varepsilon$  14900, was obtained. The characteristic absorption bands at 3044, 1636, 985 (> C = CH<sub>2</sub>) and 1743 cm<sup>-1</sup> (CO<sub>2</sub>R). Found: C63.76; H 7.46%. C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>. Calculated: C 64.27; H 7.19%.

A 7 g portion of the diester (IV) was saponified for 48 h with a solution of 5 g of potassium hydroxide in 125 ml of alcohol and 75 ml of water at 0-5°. After the usual treatment, 6.0 g of the monoethyl ester (V), m.p. 75° (ethyl acetate-hexane);  $\lambda_{\text{max}}$  (in alcohol) 231 m $\mu$ ,  $\varepsilon$  13500, was obtained. IR spectrum: 3047; 1720, and 1636 cm<sup>-1</sup>. Found: C 61.45; H 6.14%. C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>. Calculated% C 61.21; H 6.17%.

A 7 g portion of the diester (IV) was exposed at 20° for 48 h to a solution of 10 g of potassium hydroxide in 100 ml of alcohol and 50 ml of water. We isolated 2.5 g of the dicarboxylic acid (VI), which was decarboxylated when melted above 128°;  $\lambda_{max}$  (in alcohol) 231 mµ.  $\varepsilon$  15100. IR spectrum: 1726, 1637 cm<sup>-1</sup>. Found: C 57.15; H 4.95%. C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>. Calculated: C 57.14; H 4.80%.

For decarboxylation, 2.0 g of (VI) was heated gradually to 140°. The product was extracted with a solution of bicarbonate and recrystallized from a mixture of ethyl acetate-hexane. Yield 0.5 g of the dimer form of 2-methyl-cyclopentadiene-1,3-carboxylic acid (VII), m.p. 186° (with decomposition), UV and IR spectra:  $\lambda_{max}$  (in alcohol) 231 mµ,  $\varepsilon$  9200, and 1697, 1633 cm<sup>-1</sup>, correspond to the presence of a conjugated carboxyl group in the dimer form of the acid (VII). Found: C 67.15; H 6.61%. C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>. Calculated: C 67.73; H 6.50%.

Decadiene-2,8(dicis)-diyne-4,6-diol-1,10 (VIII). A mixture of 10 g of the cis-chloride (II) in 80 ml of acetone was shaken in a stream of oxygen with a mixture of 45 g cuprous chloride, 75 g ammonium chloride, 210 ml of water, and 2.2 ml of hydrochloric acid for 4 h. After the usual treatment we obtained 9.2 g of a semicrystalline mass, from which the dicis-diol (VIII) with m. p. 154-156° (ethyl acetate-hexane) was isolated;  $\lambda_{max}$  (in alcohol) 230, 238, 247, 261, 276, 293, 312 mµ;  $\varepsilon$  30400, 27000, 21000, 7300, 14400, 18100, 22200. IR spectrum: 3384 cm<sup>-1</sup> (OH), 2195, 2124 cm<sup>-1</sup> (C = C), 724 cm<sup>-1</sup> (c-CH = CH-). Found: C 73.94; H 6.28%. C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>. Calculated: C 74.05; H 6.22%. The ditrans-glycol possesses a higher extinction in the UV spectrum (by 5-8 thousand) for the same absorption maxima [5].

Dodecadiene-3,9(dicis)-diyne-5,7-tetracarboxylic-1,1,12,12 Acid (IX). A 9 g portion of the unpurified cisdiol (VIII) was treated with phosphorus tribromide, and the dibromide obtained was reacted with sodium malonic ester, as described above. After the usual treatment, the reaction product was saponified at 20° with an alcohol solution of potassium hydroxide. Extraction with a mixture of ethyl acetate-hexane isolated 3.0 g of the crystalline acid (IX), which does not melt when heated to 300°;  $\lambda_{max}$  (in alcohol) 221, 231, 238, 249, 263, 277, 294, 314 mµ,  $\varepsilon$  27800, 30100, 30100, 23100, 8770, 16000, 23500, 18600. The IR spectrum possesses an absorption band at 724 cm<sup>-1</sup> (c-CH = CH-). Found: C 57.14; H 4.73%. C<sub>16</sub>H<sub>14</sub>O<sub>8</sub>. Calculated: C 57.49; H 4.32%.

### CONCLUSIONS

The condensation of cis-1-chloropentene-2-yne-4, with sodium malonic ester was studied, and the structure of the intramolecular nucleophilic cyclization product thereby formed was demonstrated.

### LITERATURE CITED

- 1. M. V. Mavrov and V. F. Kucherov, Izv. AN SSSR, Ser. Khim., 1653, 1820 (1964).
- 2. J. B. Hendrickson, R. Rees, and J. F. Templeton, J. Amer. Chem. Soc. 66, 107 (1964).
- 3. I. Bell, R. Madronero, and M. C. Whiting, J. Chem. Soc. 3195 (1958).
- 4. I. Bell, E. R. Jones, and M. C. Whiting, J. Chem. Soc. 2597 (1957).
- 5. I. Heilbron, E. R. H. Jones, and F. Sondheimer, J. Chem. Soc. 1586 (1947).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.