SYNTHESIS OF ESTERS OF ALLENIC ACIDS

B. P. Gusev, L. A. Tsurgozen, and V. F. Kucherov

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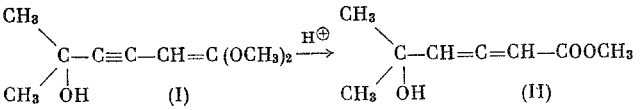
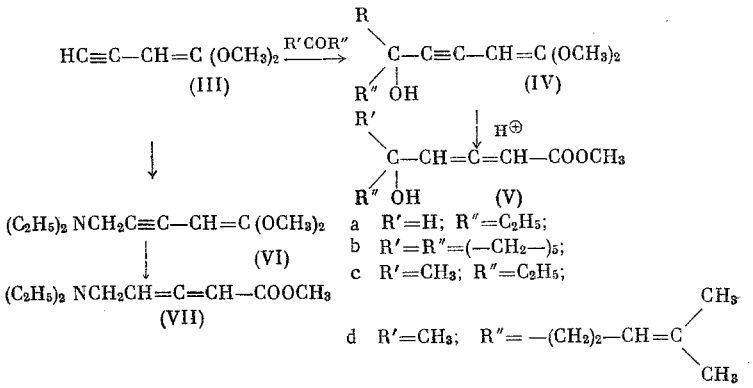
As was shown previously, the acid hydrolysis of 1,1-dimethoxy-5-methyl-5-hydroxy-1-hexen-3-yne (I) gives the methyl ester of 5-methyl-5-hydroxy-2,3-hexadienoic acid (II) in good yield



In order to check the possibility of using this reaction to synthesize other allenic hydroxyesters of similar type we studied the acid hydrolysis of a number of acetylenic acetals of general formula (IV), which were obtained by the condensation of the previously described 1,1-dimethoxy-1-buten-3-yne (III) [2] with various carbonyl compounds



It proved that in all of these cases the hydrolysis leads only to the formation of the allenic compounds (V), the structure of which followed from the data of the IR spectra (an intense absorption band at 1970 cm^{-1}). Based on the GLC and TLC data, the allenic hydroxyesters (V) obtained in this manner are pure compounds. However, both they and the starting vinylacetylenic ketals (IV) are comparatively unstable compounds, as a result of which in a number of cases we were unable to obtain satisfactory analyses for them.

The hydrolysis of amine (VI), obtained previously [1] by the Mannich reaction from 1,1-dimethoxy-1-buten-3-yne (III), also proceeds in a similar manner, with the formation of only the allenic structure (VII).

EXPERIMENTAL METHOD

Methyl Ester of 5-Hydroxy-2,3-heptadienoic Acid (Va). To the Grignard reagent, prepared from 0.38 g of Mg and 1.5 ml of C_2H_5Br in 15 ml of absolute ether, was gradually added 1.5 g of 1,1-dimethoxy-1-buten-3-yne (III) in 15 ml of THF, and the mixture was stirred for 45 min, after which 0.8 g of $CH_3CH_2 \cdot CHO$ in 5 ml of THF was added. The mixture was stirred for 3 h, decomposed with NH_4Cl solution, and the reaction product was extracted with ether and then dried over K_2CO_3. After distillation we obtained 1.4 g (62%) of (IVa) with bp 96° (0.5 mm); n_D^{20} 1.5076; ν 1640, 2220, 3400 cm^{-1}. Found: C 62.93; H 8.32%. $C_9H_{14} \cdot O_3$. Calculated: C 63.51; H 8.28%.

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For hydrolysis, 0.8 g of (IVa) was stirred at room temperature for 30 min with a mixture of 5 ml of H_3PO_4 in 15 ml of ether (1 : 20). Extraction with ether, followed by drying over $MgSO_4$ and vacuum-distillation, gave 0.6 g (82%) of (Va) with bp 75° (0.5 mm); n_D^{20} 1.4732; ν 1745, 1970, 3430 cm^{-1}. Found: C 61.13; H 7.95%. $C_8H_{12}O_3$. Calculated: C 61.51; H 7.75%.

1-(3'-Carbomethoxy-1',2'-propadienyl)-1-cyclohexanol (Vb). In a similar manner, from 1.16 g of (III) and 0.98 g of cyclohexanone was obtained 1.6 g (74%) of (IVb) with bp 130° (0.9 mm); n_D^{20} 1.5250; ν 1636, 2214, 3400 cm^{-1}. Found: C 68.12; H 8.65%. $C_{12}H_{18}O_3$. Calculated: C 68.54; H 8.63%. λ_{max} 237 nm (ethanol) (ε 12,000). The hydrolysis of (IVb) with dilute H_3PO_4 solution gave (Vb) in 78% yield, bp 116° (0.9 mm); n_D^{20} 1.5052; ν 1740, 1965, 3440 cm^{-1}. Found: C 66.70; H 8.00%. $C_{11}H_{16}O_3$. Calculated: C 67.32; H 8.22%.

Methyl Ester of 5-Phenyl-5-hydroxy-2,3-hexadienoic Acid (Vc). In a similar manner, from 2.68 g of (III) and 4 ml of $CH_3COC_6H_5$ was obtained (IVc) in 78% yield, bp 160° (0.7 mm). The hydrolysis of (IVc) with H_3PO_4 solution led to (Vc) in 67% yield, bp 135° (0.5 mm); n_D^{20} 1.5402; ν 1745, 1965, 3440 cm^{-1}. Found: C 70.71; H 6.72%. $C_{13}H_{14}O_3$. Calculated: C 71.54; H 6.47%.

Methyl Ester of 5,9-Dimethyl-5-hydroxy-2,3,8-decatrienoic Acid (Vd). Using the previously described method, from 5.67 g of (III) and 6.15 g of methylheptenone was obtained 3.99 g (35%) of (IVd) with bp 122° (0.35 mm); n_D^{20} 1.4927; ν 1640, 2220, 3550 cm^{-1}. The hydrolysis of (IVd) with H_3PO_4 solution gave 1.8 g (77%) of (Vd) with bp 95° (0.25 mm); n_D^{20} 1.4835; ν 1620, 1750, 1970, 3440 cm^{-1}. Found: C 68.87; H 9.00%. $C_{13}H_{20}O_3$. Calculated: C 69.61; H 8.99%.

Methyl Ester of 5-(N,N-Diethylamino)-2,3-pentadienoic Acid (VII). For reaction, we took 2.83 g of the previously described [2] (VI) and stirred it for 45 min with a mixture of 10 ml of H_3PO_4 and 20 ml of ether (1 : 20). After good extraction with ether, followed by drying over $MgSO_4$ and vacuum-distillation we obtained 1.98 g (75%) of (VII) with bp 62° (0.5 mm); n_D^{20} 1.4790; ν 1730, 1960 cm^{-1}. Found: N 7.42%. $C_{10}H_{17}O_2N$. Calculated: N 7.64%.

CONCLUSIONS

Starting with 1,1-dimethoxy-1-buten-3-yne, a method was proposed for the synthesis of the esters of δ-hydroxyallenic acids and of a 5-dialkylamino-2,3-pentadienoic acid.

LITERATURE CITED

1. B. P. Gusev, L. A. Tsurgozen, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 141 (1971).
2. B. P. Gusev and V. F. Kucherov, USSR Patent No. 244336 (1968); Byull. Izobr., No. 18, 28 (1969).