Studies on the Synthesis of Massoi-lactone and its Homologues. Part II. Synthesis of Nonyn-1-ol-4-carboxylic acid-1-lactone (Massoi-lactone)

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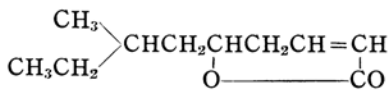
(Received August 23, 1955)

The main component of the essential oil of Massooi, the bark of Massoia aromatica Becc., is a lactone[1]. S. Abe named it "Massoi-lactone" and proposed its structural formula[1].



Afterwards, a part of this formula, outside the lactone ring was revised by Th. Meijer[2]

1) S. Abe, *J. Chem. Soc. Japan*, 58, 246-248 (1937); 733-738 (1937).

2) Th. Meijer, *Rec. trav. chim.*, 59, 191-201 (1940.)

to be a straight chain. S. Abe and K. Sato[3] also confirmed the new structure. Simultaneously, we undertook to synthesize Massoi-lactone and its homologues and prepared decene-1-ol-4-carboxylic acid-1-lactone[4], having one more methyene group than real Massoi-lactone has.

$$CH_3(CH_2)_5\underset{\displaystyle O\text{————————}}{CH}CH_2CH=\underset{\displaystyle CO}{CH}$$

The Massoi-lactone was prepared in the same way. *n*-Nonyn-1-ol-4 (I) was obtained by the Reformatskys reaction from *n*-hexanal and propargyl bromide as a colorless liquid, b. p. 72–73°/6 mm. The etherial solution of this alcohol was added to 2 moles of ethyl magnesium bromide, forming a magnesium compound(II), accompanied with an evolution of ethylene.

The mixture of this magnesium compound and excess of dry ice was shaken for twenty-four hr. in an autoclave under 20 atm. at room temperature. After decomposing the content with dilute solfuric acid, *n*-nonyn-1-ol-4-carboxylic acid(III) thus formed was extracted with ether and isolated.

$$CH_3(CH_2)_4CHO + BrCH_2C\equiv CH \xrightarrow{Zn} CH_3(CH_2)_4\underset{\displaystyle OH}{CH}CH_2C\equiv CH \xrightarrow{2C_2H_5MgBr}$$

(I)

$$CH_3(CH_2)_4\underset{\displaystyle OMgBr}{CH}CH_2C\equiv CMgBr \xrightarrow{CO_2(solid)} CH_3(CH_2)_4\underset{\displaystyle OH}{CH}CH_2C\equiv CCOOH \xrightarrow[Pd\text{-}BaSO_4]{H_2}$$

(II) (III)

$$CH_3(CH_2)_4\underset{\displaystyle O\text{————————}}{CH}CH_2CH=\underset{\displaystyle CO}{CH}$$

The methanol solution of this acid was partially hydrogenated with hydrogen at room temperature in the presence of Pd-$BaSO_4$ (5% Pd). After removing the solvent and distilling under reduced pressure, *n*-nonene-1-ol-4-carboxylic acid-1-lactone (Massoi-lactone) (IV) was obtained as a colorless, fragrant smeling liquid, b.p. 147–149°/8mm, $d_D^{20}=0.9787$, $n_D^{20}=1.4669$.

Experimental

Propargyl bromide.—Propargyl bromide was prepared from propargyl alcohol and phosphorus tribromide according to the method by A. Kirrmann[5]. b.p. 81–83°. $d_4^{20}=1.5970$, $n_D^{02}=1.4952$, yield 75.8%.

Nonyn-1-ol-4 (I).—Into a three necked flask equipped with a reflux condenser, a dropping funnel and an air tight stirrer, 30 g. of activated zinc powder and 60 g. of dry benzene were put and heated to boiling on a water bath. A mixture of 45 g. of *n*-hexanal, 45 g. of propargyl bromide and 90 g. of ether was added drop by drop from the dropping funnel while the liquid was kept at gentle boiling, so as to avoid adding too much of the mixture at a time until reaction started. After the whole mixture was added, the content of the flask was refluxed for further 1.5 hr. The reaction mass was cooled and decomposed with 270 cc. of 10% acetic acid. The lower acqueous layer was extracted with ether. The upper benzene-ether layer and the extract were put in together, washed with a saturated solution of sodium bicarbonate, dehydrated over anhydrous sodium sulfate. After removing the solvent and distilling in vacuo, nonyn-1-ol-4 was obtained as a colorless liquid. b.p. 72–73°/6 mm, $d_4^{20}=0.8682$, $n_D^{20}=1.4480$, yield 25 g. 47.2%. M. R., Obs.: 43.24, Calcd.: 43.29.

Anal. Found: C, 76.65; H, 11.29. Calcd. for $C_9H_{16}O$: C, 77.14; H, 11.42%.

Nonyn-1-ol-4-carboxylic acid-1.—To the Grignard's reagent prepared from 6 g. of magnesium and 17 g. of ethyl bromide, a mixture of nonyn-1-ol-4 and 60 cc. of benzene was added drop by drop. After ethylene ceased to evolve, the whole content was put in an autoclave together with 100 g. of dry ice and shaken for twenty-four hr. at room temperature. The pressure gauge indicated 20 atm.

The reaction mass was decomposed with 86 cc. of 15% sulfuric acid and crushed ice. The layers were separated. The lower acqueous layer was extracted with ether. The upper benzene-ether layer and the extract were put together and extracted twice with a saturated acqueous solution of sodium bicarbonate. To the alkalline extract, 15% sulfuric acid was added until no oily substance separated. The oil was extracted with ether. After dehydrating over anhydrous sodium sulfate and removing the solvent, a colourless and viscous acidic liquid was obtained. It solidifies on cooling with dry ice but melted at room temperature. Yield 10.0 g. 44.8%. Molecular weight (by titration), Found: 186.6, Calcd. for $C_{10}H_{16}O_3$: 184.2. From the benzene-ether layer 3 g. of unreacted nonyn-1-ol-4 was recovered.

Nonene-1-ol-4-carboxylic acid-1-lactone.—Six grams of nonyn-1-ol-4-carboxylic acid-1 was

3) S. Abe and K. Sato, *J. Chem. Soc. Japan*, **75**, 952-953 (1954).
4) S. Abe and K. Sato, *J. Chem. Soc. Japan*, **75**, 953-955 (1954).
5) A. Kirrmann, *Bull. soc. chim.*, **39**, 698 (1926).

dissolved in 60 cc. of methanol, and after adding 2 g. of Pd-$BaSo_4$ (5% Pd). was partially hydrogenated with 0.66 l. of hydrogen (90% of the theoretical amount) at room temperature with constant shaking. After filtering off the catalyser and removing the solvent in vacuo, 50 cc. of benzene was added to the residue and the solvent was removed again in vacuo. Finally the residue was distilled in vacu. Nonene-1-ol-4-carboxylic acid-1-lactone was obtained as a colorless liquid, b. p. 147–149°/8 mm. Yield 3.4 g. (70%). $d_4^{20}=0.9787$. $n_D^{20}=1.4669$. M. R., Obs.: 47.75, Calcd.: 47.37.

Anal. Found: C, 71.18; H, 9.60. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.60%.

Summary

The Massoi-lactone (nonyn-1-ol-4-carboxylic acid-1-lactone), the main component of the essential oil of Massoi-bark was synthesized from *n*-hexanal and propargyl bromide.

A part of the cost of this study has been defrayed from the Scientific Research Expenditure of the Ministry of Education. Tue authors wish to express their sincere thanks to Mr. S. Kikuchi for his help during the course of this experiment.

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