Chemistry

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1957

SovietRxiv

Abstract

Full Text

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OXIDES OF SOME DERIVATIVES OF α-PINENE AND THEIR ISOMERIZATION

In a series of previous works it was established that the oxide of α-pinene and of other bicyclic terpenes undergoes complex transformations under the influence of various reagents. Thus, under the influence of zinc bromide and certain other catalysts, α-pinene oxide is converted into the isomeric campholenic aldehyde. Such isomerization is accompanied by a profound rearrangement of the original skeleton of α-pinene oxide ([1–2]). It had been found still earlier ([3]) that cyclohexene oxide is readily isomerized into cyclopentane aldehyde.

In the work of B. A. Arbuzov, Z. G. Isaeva, and E. G. Kataev ([4]) it was shown that the introduction of certain substituents into the nucleus of cyclohexene oxide increases the stability of the oxide to such an extent that it was not possible to isomerize the indicated derivatives. From this point of view, it seemed of interest to obtain oxides of various derivatives of α-pinene and to study their capacity for isomerization.

We synthesized—by oxidation with acetyl hydroperoxide of the corresponding derivatives of α-pinene—oxides containing the myrtenyl radical, and carried out their isomerization reactions under the influence of zinc chloride:

$$\text{(myrtenyl derivative with } CH_2X) + CH_3COOOH \longrightarrow \text{(corresponding oxide)} \xrightarrow{ZnBr_2} \text{(aldehyde with CHO)}$$

where $X = OCH_3$, OC_3H_7-iso, OC_4H_9, OC_4H_9-iso, Cl, $OCOCH_3$, C_2H_5, C_3H_7-iso, OH.

Derivatives of α-pinene were obtained from myrtenyl chloride by the action of the corresponding reagents. The constants of derivatives not described in the literature—

Table 1

Mol. form. no.	B.p., °C	Pressure, mm	d_0^{20}	n_D^{20}	MR_D, calc.	MR_D, found	C %, calc.	C %, found	H %, calc.	H %, found	Yield, %
I	105–106	15	0.9217	1.4710	59.49	58.90	80.41	80.02	11.34	10.90	29.5
II	104–105	10	0.9046	1.4670	64.10	63.80	80.76	80.57	11.54	11.57	14.0
III	115–117	12	0.9025	1.4659	64.10	63.72	80.76	80.38	11.54	11.53	24.0

Note.

I : myrtenyl $CH_2OCH(CH_3)_2$ derivative,
II : myrtenyl $CH_2OCH_2CH(CH_3)_2$ derivative,
III : myrtenyl $CH_2OC_4H_9$ derivative.

Table 2

Formula no.	B.p., °C	Pressure, mm	d_0^{20}	n_D^{20}	MR_D, calc.	MR_D, found	C %, calc.	C %, found	H %, calc.	H %, found	Yield, %
I	70–72	7	0.9616	1.4810	53.14	53.22	80.00	79.90	10.55	10.30	44.78
II	122–124	8	0.9361	1.4710	57.75	57.90	80.41	80.28	11.34	11.74	72.6
III	87–90	2	1.1086	1.4980	48.77	49.29	64.34	63.74	8.04	8.57	29.24
IV	98–104	6	1.0788	1.4900	45.34	45.06	74.44	74.07	9.52	9.70	56.36
V	112–114	6	1.0841	1.4785	54.79	54.87	68.57	68.06	8.57	8.81	40.5
VI	75–76	4	1.0240	1.4770	50.16	50.22	72.52	72.05	9.89	9.67	49.2
VII	108–110	10	1.0197	1.4828	59.40	58.85	74.28	73.86	10.47	10.62	44.4

Formula no.	B.p., °C	Pressure, mm	d_0^{20}	n_D^{20}	MR_D, calc.	MR_D, found	C %, calc.	C %, found	H %, calc.	H %, found	Yield, %
VIII	108–110	16	0.9726	1.4660	64.02	63.78	75.04	74.67	10.71	10.87	36.0
IX	110–114	20	0.9784	1.4740	64.02	64.35	75.04	74.53	10.71	10.76	28.8

Note.

I: α-pinene oxide derivative with $-CH_2CH_2CH_3$ substituent.
II: α-pinene oxide derivative with $-CH_2CH(CH_3)_2$ substituent.
III: α-pinene oxide derivative with $-CH_2Cl$ substituent.
IV: α-pinene oxide derivative with $-CH_2OH$ substituent.
V: α-pinene oxide derivative with $-CH_2OC(O)CH_3$ substituent.
VI: α-pinene oxide derivative with $-CH_2OCH_3$ substituent.
VII: α-pinene oxide derivative with $-CH_2OCH(CH_3)_2$ substituent.
VIII: α-pinene oxide derivative with $-CH_2OC_4H_9$ substituent.
IX: α-pinene oxide derivative with $-CH_2OCH_2CH(CH_3)_2$ substituent.

Table 3

Formula no.	B.p., °C	Pressure, mm	d_0^{20}	n_D^{20}	MR_D, calc.	MR_D, found	C %, calc.	C %, found	H %, calc.	H %, found	Yield, %
I	112–114	8	0.9098	1.4745	59.58	59.87	80.41	79.81	11.34	10.88	29.65
II	92–95	6	0.9926	1.4806	51.98	52.08	72.52	72.90	9.89	9.71	29.22
III	102–104	2	1.0600	1.4820	56.61	56.52	68.54	68.41	8.62	8.66	25.26
IV	104–106	9	1.0912	1.5086	50.59	50.66	64.34	64.90	8.04	7.81	29.00

Note.

I: campholenic aldehyde derivative with $-CH_2CH(CH_3)_2$ and $-CHO$ substituents.
II: campholenic aldehyde derivative with $-CH_2OCH_3$ and $-CHO$ substituents.

III: campholenic aldehyde derivative with $-CH_2OC(O)CH_3$ and $-CHO$ substituents.
IV: campholenic aldehyde derivative with $-CH_2Cl$ and $-CHO$ substituents.

···are given in Table 1. The properties of the oxides obtained by us that have not been described in the literature are given in Table 2. Some of the oxides obtained were subjected to the isomerization reaction. The isomerization of the oxides obtained was carried out in the presence of zinc chloride as catalyst. As a result, the corresponding derivatives of campholenic aldehyde were isolated. The properties of the obtained derivatives of campholenic aldehyde are presented in Table 3.

The structure of the obtained derivatives of campholenic aldehyde was proved by their physical properties (MR_D), by determination of the presence of a double bond, and by oxidation with silver oxide to the corresponding substituted campholenic acid. The substituted campholenic acids were analyzed in the form of their silver salts.

As can be seen from the data presented, the isomerization of the studied derivatives of α-pinene oxide proceeds analogously to the isomerization of α-pinene oxide and leads to the formation of substituted campholenic aldehyde. The isomerization proceeds less smoothly, and the yield of the corresponding substituted derivatives of campholenic aldehyde is 25–30%.

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Received
13 X 1956

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Note: Figure translations are in progress. See original paper for figures.