

# Synthesis and odor properties of carene and carane derivatives

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In addition to  $\alpha$ -pinene, (+)-car-3-ene *1* is the main component of turpentine obtained from the *Pinus silvestris* pine. Its content in Polish, German, and Russian turpentines is 15-41%.<sup>1</sup> Until now, (+)-car-3-ene has been insufficiently used for the syntheses of odor compounds. Only two such compounds are manufactured on a commercial scale: 4-hydroxymethyl-2-carene *2*, having a flower odor with a fruit note, and its acetate with a herb-flower odor, the "turiol" and turiol acetate of Dragoco.<sup>2</sup> The syntheses of several nitriles, derivatives of carene and carane, patented recently in Germany, also deserve attention.<sup>3</sup> Interesting prospects are seen using (+)-car-3-ene for the synthesis of l-menthol by the series of reactions worked out by Sukh Dev and coworkers.<sup>4</sup>

An extensive review of the possible uses of car-3-ene for the syntheses of odor compounds has recently been published by Verghese.<sup>5</sup> The purpose of this report is to detail the syntheses of novel 4-substituted derivatives of carene and carane, and studies of their sensory (odorous) properties. The compounds were prepared from (+)-car-3-ene in a series of processes shown in figure 1.

In the first stage of the synthesis, (+)-car-3-ene *1* separated from Polish balsamic turpentine was changed, in the Prins reaction, to a mixture of acetates of 4-hydroxymethyl-2-carene *3* and 4-hydroxymethyl-3(10)-carene *4*. Hydrolysis of this mixture resulted in a mixture of 4-hydroxymethyl-2-carene *2* and 4-hydroxy-

methyl-3(10)-carene *5* in a ratio of 94:6.<sup>6</sup> From alcohols *2* and *5*, the respective alkoxynitriles *6* and *7* were prepared by reaction with acrylonitrile in an alkaline medium.<sup>7</sup> On the other hand, by the oxidation of alcohols *2* and *5*, an 83:17 mixture of 4-formyl-2-carene *8* and 4-formyl-3(10)-carene *9* was obtained. From the mixture of these aldehydes, their acetals with ethanediol-1,2 *10* and *11* were prepared.

4-Formyl-3-carene *13* was prepared by the decomposition of the semicarbazone of 4-formyl-2-carene *12* in a 3% boiling aqueous solution of oxalic acid. In the second stage, the mixture of homocarenols *2* and *5* was hydrogenated catalytically with Raney Ni to 4-hydroxymethylcarane *14*. This compound was further used to synthesize the following compounds in a series of reactions analogous to those described above: alkoxynitrile *15*, 4-hydroxymethylcarane acetate *16*, 4-hydroxymethylcarane propionate *17*, and 4-formylcarane *18* and its acetals with ethyl orthoformate *19*, ethanediol-1,2 *20*, and propane-1,2,2 *21*.

The purity of the compounds was checked by GC and their structure was determined by spectral methods: IR, NMR, and MS. The odor characteristics of the compounds are given in Table I.

Results obtained by the comparison of odors of the carene and carane derivatives show that the decisive effect on the odor nature seems to come from functional groups.

The derivatives of 4-substituted carane show

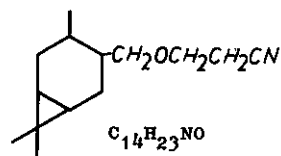
**Table I. Odor Characteristics of the Prepared Compounds**

Compound formula	Boiling point °C/mmHg	Odor characteristics
<p><u>3</u> / <u>4</u>  <math>C_{13}H_{20}O_2</math>  <math>M=208,29</math></p>	91-93/1,5	herb-flower odor [2]
<p><u>2</u> / <u>5</u>  <math>C_{11}H_{18}O</math>  <math>M=166,24</math></p>	86-87/0,8	flower odor with a fruit note [2]
<p><u>6</u> / <u>7</u>  <math>C_{14}H_{21}NO</math>  <math>M=219,33</math></p>	102-103/0,2	weak odor
<p><u>8</u> / <u>9</u>  <math>C_{11}H_{16}O</math>  <math>M=164,23</math></p>	54-56/0,7	verbena odor with balsamic-woody note
<p><u>10</u> / <u>11</u>  <math>C_{13}H_{20}O_2</math>  <math>M=208,29</math></p>	82-84/1,5	intensive, fresh green-kumina odor with flowery note
<p><u>13</u>  <math>C_{11}H_{16}O</math>  <math>M=164,23</math></p>	84-86/3	fresh, strong kumina like odor
<p><u>14</u>  <math>C_{11}H_{20}O</math>  <math>M=168,26</math></p>	92-93/1,5	terpinolene like odor

Table I continues on page 54

# Carene and carene derivatives

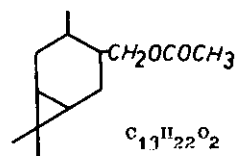
**Table I**  
Continued



15

110-112/0,4

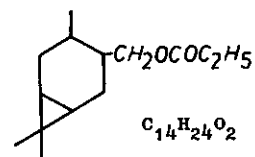
weak, woody "soily" odor



16

98-99/2

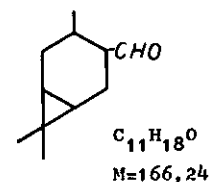
intensive balsamic-woody odor



17

88-89/0,4

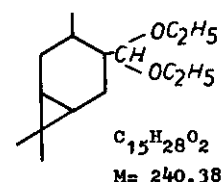
delicate, woody, patchouli-cedren, odor, with fresh green note



18

100/10

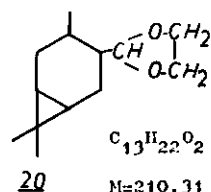
balsamic odor with pepper shade



19

80-81/0,4

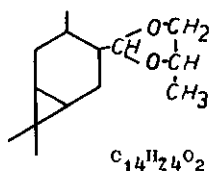
fresh, green, woody, fruit-pear odor



20

91-94/1,3

woody, fresh odor balsamic with very light anise note

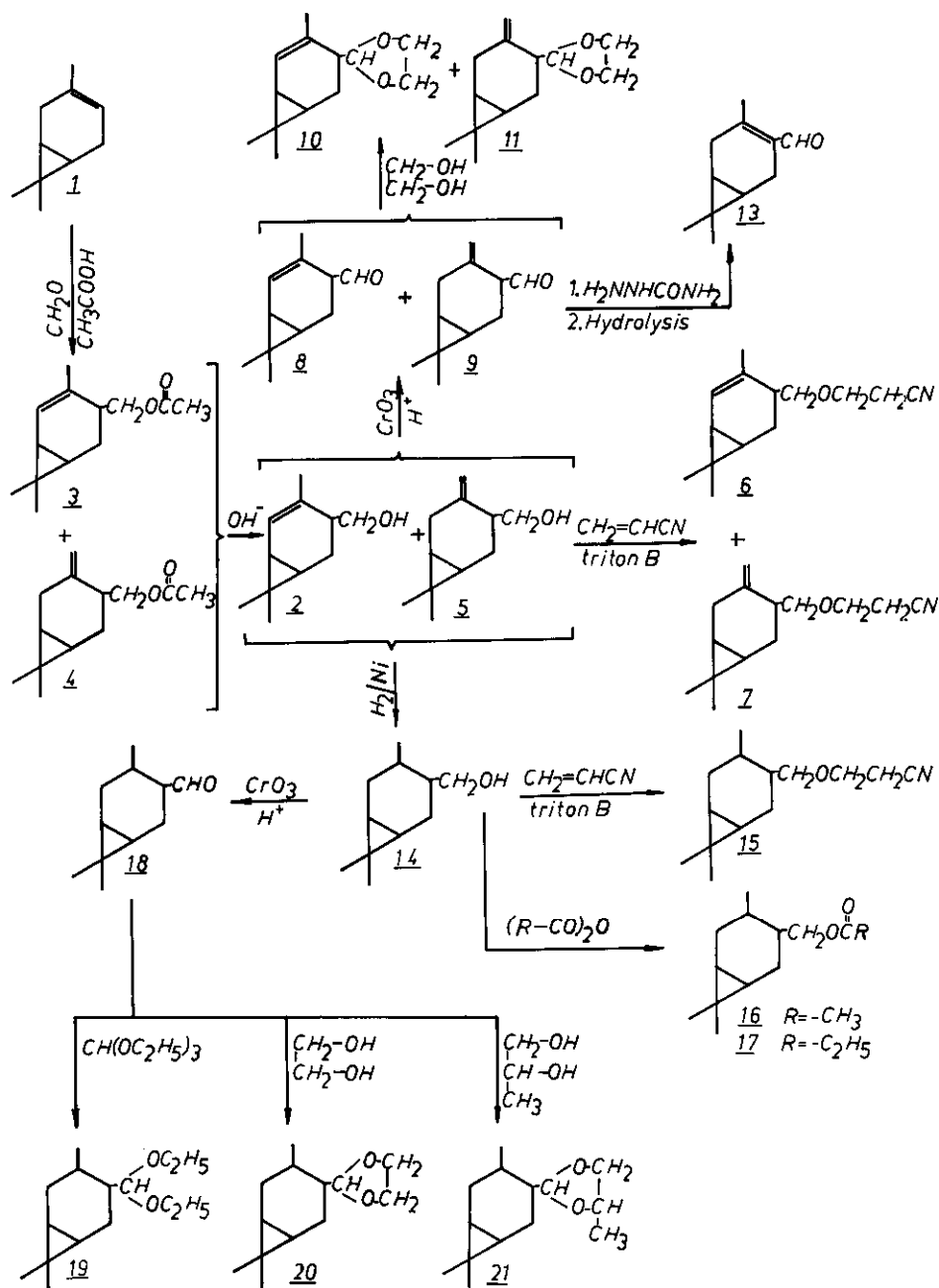


21

102-104/0,2

light coumarin odor with menthol note, fresh, green, woody

Figure 1



an odor which is milder and finer than that of the respective derivatives of carene. It can be generally stated that the introduction of a side chain containing 1-4 carbon atoms and a functional group (alcohol, carbonyl, ester or acetal) into position 4 of the carene or carane system makes it possible to synthesize several new compounds possessing interesting odor properties. Some of them may advantageously enrich the range of perfume materials manufactured from car-3-ene.

References

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