

UDC 547.538.547.568.547.572

Heino RANG\*, Sirje VIITMAA\*, and Koit LÄATS\*

### SYNTHESIS AND FRAGRANT CHARACTERISTICS OF 1-PHENYLDIMETHYLHEXENE 1-OXY AND 1-OXO DERIVATIVES

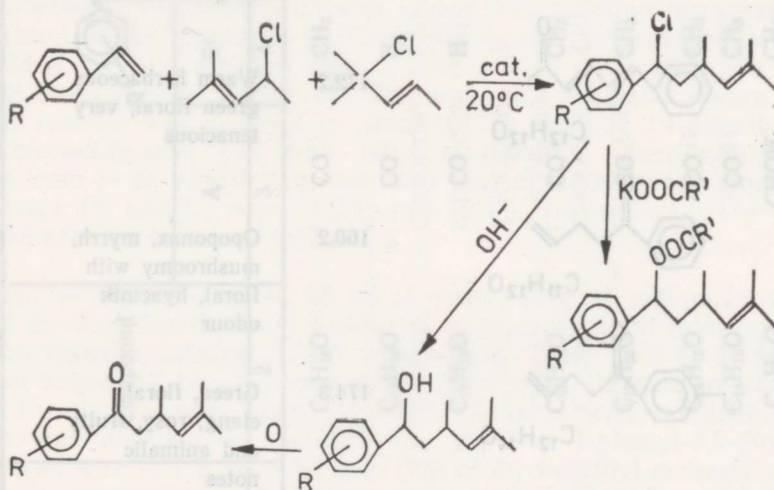
1-Phenyl-4-pentene-1-one was first synthesized from 1-phenylalkene-1-ones and described by Bayer and Perkin in 1883[1]. Of phenylalkenones as fragrances Arctander described two derivatives[2, 3] having a sweet odour and phenylalkadienone[4] with a floral green odour.

The main methods for synthesizing 1-phenylalkene-1-ones are alkylation of phenylketones with 2-alkene-1-halides[1, 5, 6] or condensation of ketones with aldehydes[7]. Darzens was the first to synthesize 1-phenylalkene-1-ones by alkylation of aromatic hydrocarbons with unsaturated acid chlorides[8]. The condensation of acetophenone with ketones in the presence of MgBr-anilide[9] is interesting from a historical viewpoint.

In our method of synthesizing 1-phenylalkene-1-ones the molecular skeleton was constructed by the addition of phenylalkenes (e.g. styrene) to allyl halides (e.g. 4-chloro-2-pentene) in the presence of Lewis catalysts[10]. The oxy derivatives were synthesized by the hydration of the halide products and the oxo derivatives by the oxidation of oxy products [10-12].

Our method enables to synthesize structures (for example compounds synthesized and described in this paper) which are impossible to obtain by alkylation of ketones with 1-chloro-2-alkenes. Therefore, it is possible to directly synthesize esters and alcohols which are fragrances from the haloadduct in the first step.

We have shown earlier that the 3-methyl group of the alkene chain affords a compound with a very powerful and tenacious green odour[11]. In this work, the synthesis of 3,5-dimethyl derivatives was carried out according to the following scheme:



\* Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE0108 Tallinn, Estonia.

and it is shown that the two methyl groups in positions 3 and 5 increase the intensity of the odour even more. We have synthesized a high-molecularmass fragrance (compound 10 in Table 1) with a very powerful odour.

We used a technical mixture of methylchloropentenes (70% of 2-methyl-4-chloro-2-pentene and 30% of 4-methyl-4-chloro-2-pentene) because it is technologically available and much cheaper than pure isomers.

In Table 1, all the known fragrances of the oxo and oxy derivatives of phenylalkene and their fragrant characteristics are presented. Compounds 6—18 and 20—24 have been synthesized according to the scheme worked out by the present authors.

The physical characteristics and  $^{13}\text{C}$  NMR spectra of the compounds synthesized in this work are presented respectively in Tables 2 and 3—5. The  $^{13}\text{C}$  NMR spectra were interpreted on the basis of [13].

Table 1a

Fragrant characteristics of oxo and oxy derivatives of phenylalkenes

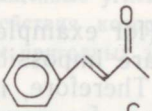
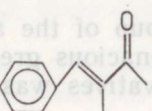
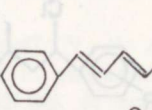
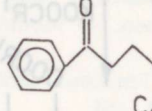
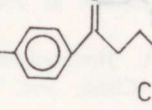
No.	Compound	Mol. mass	Fragrant characteristics	References
1	 $\text{C}_{10}\text{H}_{10}\text{O}$	146.2	Sweet, but rather pungent	[2]
2	 $\text{C}_{11}\text{H}_{12}\text{O}$	160.2	Sweet, fruity caramel, berrylike of good tenacity	[3]
3	 $\text{C}_{12}\text{H}_{12}\text{O}$	172.2	Warm herbaceous green floral, very tenacious	[4]
4	 $\text{C}_{11}\text{H}_{12}\text{O}$	160.2	Opoponax, myrrh, mushroomy with floral, hyacinth odour	[1, 6]
5	 $\text{C}_{12}\text{H}_{14}\text{O}$	174.3	Green, floral, elang, rosy, fruity and animalic notes	[6]



Table 1b

## Fragrant characteristics of oxo and oxy derivatives of phenylalkenes

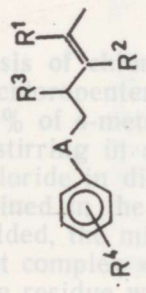
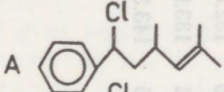
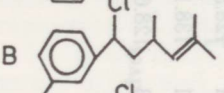
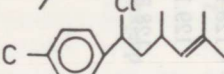
No.	Compound								Mol. mass	Fragrant characteristics	References
		A	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>					
1	2	3	4	5	6	7	8	9	10		
6	C <sub>13</sub> H <sub>16</sub> O	CO	CH <sub>3</sub>	H	H	H	H	188.3	Geranium, sharp, tenacious (on paper for 7 days)	[5, 10]	
7	C <sub>13</sub> H <sub>16</sub> O	CO	H	H	CH <sub>3</sub>	H	H	188.3	Green, herbaceous, powerful, tenacious (on paper for 15 days)	[11]	
8	C <sub>14</sub> H <sub>18</sub> O	CO	H	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	202.3	Green, fresh with a bitter undertone. Very powerful and tenacious (on paper for 20 days)	[11]	
9	C <sub>14</sub> H <sub>18</sub> O	CO	CH <sub>3</sub>	H	CH <sub>3</sub>	H	H	202.3	Green, dill roots, very powerful and tenacious (on paper for 25 days)	This paper	
10	C <sub>15</sub> H <sub>20</sub> O	CO	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	216.3	Green, fresh, orris, very powerful and tenacious (on the paper for 30 days)	This paper	
11	C <sub>14</sub> H <sub>18</sub> O	CO	CH <sub>3</sub>	H	H	CH <sub>3</sub>	CH <sub>3</sub>	202.3	Geranium	[10]	
12	C <sub>14</sub> H <sub>18</sub> O	CO	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	202.3	Geranium	[10]	
13	C <sub>14</sub> H <sub>20</sub> O	CHOH	CH <sub>3</sub>	H	CH <sub>3</sub>	H	H	204.3	Bergamot, a weak shade of green	This paper	
14	C <sub>15</sub> H <sub>22</sub> O	CHOH	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	218.3	Floral, fruity with a bitter undertone	This paper	
15	C <sub>13</sub> H <sub>18</sub> O	CHOH	H	H	CH <sub>3</sub>	CH <sub>3</sub>	H	190.3	Green, fatty	[14]	

Table 1b continued

1	2	3	4	5	6	7	8	9	10
16	C <sub>14</sub> H <sub>20</sub> O	CHOH	H	H	CH <sub>3</sub>	CH <sub>3</sub>	204.3	Fruity, bird-cherry	[14]
17	C <sub>13</sub> H <sub>18</sub> O	CHOH	CH <sub>3</sub>	H	H	H	190.3	Floral, geranium	[5]
18	C <sub>14</sub> H <sub>20</sub> O	CHOH	CH <sub>3</sub>	H	H	CH <sub>3</sub>	204.3	Floral, orris, woody with a green undertone	[15]
19	C <sub>15</sub> H <sub>20</sub> O <sub>2</sub>	CHOOCCCH <sub>3</sub>	CH <sub>3</sub>	H	H	H	232.4	Floral, geranium	[5]
20	C <sub>16</sub> H <sub>22</sub> O <sub>2</sub>	CHOOCCCH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	246.4	Floral, rosy, lily, hyacinth, patchouly	[16]
21	C <sub>15</sub> H <sub>20</sub> O <sub>2</sub>	CHOOCCCH <sub>3</sub>	H	H	CH <sub>3</sub>	H	232.4	Floral, gardenia	[14]
22	C <sub>16</sub> H <sub>22</sub> O <sub>2</sub>	CHOOCCCH <sub>3</sub>	H	H	CH <sub>3</sub>	CH <sub>3</sub>	246.4	Green	[14]
23	C <sub>16</sub> H <sub>22</sub> O <sub>2</sub>	CHOOCCCH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	H	246.4	Floral with a green undertone	This paper
24	C <sub>17</sub> H <sub>24</sub> O <sub>2</sub>	CHOOCCCH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	260.4	Floral with a green undertone	This paper

## Characterization of the compounds synthesized

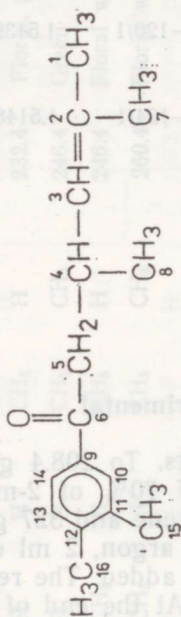
No.	B. p., °C/Torr	$n_D^{20}$	$d_4^{20}$	Purity by GLC, %	
9	101—102/2	1.5205	0.9583	95.2	
10	124—126/2	1.5204	0.9645	95.1	
13	96—97/1	1.5143	0.9510	95.2	
14	115—120/1	1.5141	0.9405	91.3	
23	101—102/1	1.4979	0.9623	93.0	
24	110/1	1.5102		90.0	
A		105—108/4	1.5158	0.981	93.0
B		118—120/1	1.5139	0.9726	92.0
C		120—124/1	1.5148	0.9699	90.1

## Experimental

**Synthesis of chloroaddition products.** To 208.4 g of styrene, 118.5 g of methylchloropentenes, a mixture of 70% of 2-methyl-4-chloro-2-pentene and 30% of 4-methyl-4-chloro-2-pentene and 327 g of dichloroethane and, while stirring in an atmosphere of argon, 2 ml of a 2% solution of tin tetrachloride in dichloroethane was added. The reaction temperature was maintained in the range 0—30°C. At the end of the reaction carbamide was added, the mixture was stirred, then settled and carbamide with the catalyst complex was filtered off. The unreacted substances were distilled off. The residue was distilled in vacuum. The yield of 2,4-dimethyl-6-phenyl-6-chloro-2-hexene (A) was 140.4 g (58.6%) when synthesis was started from 3- or 4-methylstyrene, and that of 6-(3- or 4-methyl) phenyl derivatives (B and C) was 51.2% and 42.4%, respectively. The products obtained are characterized in Table 2.

**Synthesis of oxy derivatives.** 55 ml of water, 14 g of sodium bicarbonate, 25 g of 2,4-dimethyl-6-phenyl-6-chloro-2-hexene, 25 ml of toluene, and 2 g of phase transfer catalyst TEBA were stirred at 95—100°C in an atmosphere of argon till the disappearance of the bond chlorine in the organic layer. The layers were then stratified. Toluene was distilled and the residue was distilled in vacuum. The yield of 1-phenyl-3,5-dimethyl-4-hexene-1-ol was 18.1 g (80.9%) and that of 3-, 4-methyl derivatives 79.7% and 79.1%, respectively. The latter two were synthesized from 2,4-dimethyl-6-(3- or 4-methylphenyl)-6-chloro-2-hexene. The products are characterized in Table 2 (Nos. 13 and 14, respectively).



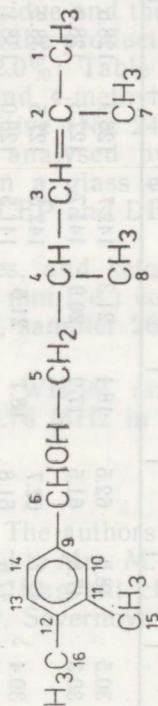
Chemical shifts of  $^{13}\text{C}$  NMR spectrum of oxo derivatives

No. of compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16
9	25.7	130.8	129.8	29.5	46.3	199.8	17.8	21.2	137.6	128.1	128.5	132.8	128.5	128.1	—	—
10a	25.7	130.5	129.9	29.4	46.2	199.6	17.9	21.2	137.5	129.1	138.1	133.5	128.4	125.4	20.5	—
10b	25.7	130.5	129.9	29.5	46.0	199.1	17.9	21.2	135.0	128.3	128.6	143.3 <sup>a</sup>	128.6	128.8	—	21.2

Table 3

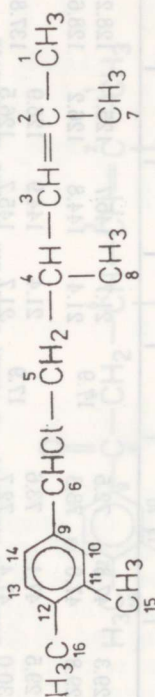
Table 3 continued

Table 4

Chemical shifts of  $^{13}\text{C}$  NMR spectrum of oxy derivatives

No. of compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16
13 threo erythro	25.8	130.9 131.0	130.6	29.3 29.8	47.3 47.0	72.5 73.3	17.9	21.7 21.4	145.7 144.8	125.7 126.2	128.2 128.6	127.1 127.3	128.2 128.6	—	—	—
14a threo erythro	25.8	130.5 131.0	131.2 130.8	29.5 30.0	47.1 47.4	73.6 72.7	17.9	21.4 21.7	144.9 145.7	126.9 126.5	137.8	128.1 128.0	128.3 122.8	21.4	—	—
14b threo erythro	25.8	130.5 130.9	131.2 130.8	29.5 —	47.2 47.4	73.7 72.5	17.9	21.4 21.7	142.0 142.7	126.2 125.7	129.0	136.9 136.7	126.2 125.7	—	—	21.0

Table 5

Chemical shifts of  $^{13}\text{C}$  NMR spectrum of chloro derivatives

No. of compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16
A threo erythro	25.8 25.7	132.1 131.1	129.6 129.6	30.5 30.3	48.0 47.8	62.5 61.5	18.1 17.9	21.3 20.9	142.7 141.7	126.9 127.3	128.5 128.0	126.9 128.0	128.5 128.5	126.9 127.3	—	—
B threo erythro	25.9 25.8	132.2 131.1	129.5 129.6	30.4	47.7 47.6	62.7 61.8	18.1	21.5	142.5 141.5	127.5 128.0	138.2 138.1	128.8 128.9	128.5 128.5	123.9 124.3	21.1	—
C threo erythro	25.9 25.8	132.2 131.1	129.5 129.6	30.4	47.7 47.6	62.6 61.7	18.1	21.5	139.6 139.9	126.8 127.2	129.2	137.8 <sup>a</sup> 137.9	129.2 127.2	126.8 127.2	—	20.9



**Synthesis of oxo derivatives.** To a mixture of water (50 ml), sodium bichromate (9 g), and conc. sulphuric acid (5.5 ml) 7 g of 3,5-dimethyl-1-phenyl-4-hexene-1-ol was added dropwise while stirring at 0°C. Then the mixture was stirred at 40°C for 1 hour. The resulting product was poured into ice water. The organic layer was extracted with toluene, washed with a 1% sodium carbonate solution, and then with brine to a neutral reaction. Toluene was evaporated and from the residue 3,5-dimethyl-1-phenyl-4-hexene-1-one was distilled in vacuum (yield 5.4 g or 78.3%). The characteristics of the oxo derivatives are presented in Table 2 (Nos. 9 and 10). The yields of 3-, 4-methyl derivatives were 77.7% and 61.0%, respectively. These two were synthesized from 3,5-dimethyl-1-(3- or 4-methylphenyl)-4-hexene-1-ol.

**Synthesis of acetates.** 22.3 g of 2,4-dimethyl-6-phenyl-6-chloro-2-hexene and 20 g of potassium acetate in 200 ml of dimethylformamide (DMFA) were stirred at 100°C, controlled with GLC, DMFA was distilled. Toluene was added to the residue and the mixture was washed with water. Toluene was evaporated and the product was distilled from the residue in vacuum (yield 19.1 g or 72.0%; Table 2, No. 23). If synthesis is started from 2,4-dimethyl-6-(3- and 4-methylphenyl)-6-chloro-2-hexene, the product is methylphenyl derivative (No. 24) and the yield is 67.2%.

Chlorides were analysed by means of a Chrom 5 chromatograph (Czechoslovakia) on a glass capillary column (41 m × 0.25 mm i. d.) coated with a 4:1 TCEP and DEGS at 100°C, sampler 180°C, carrier gas Ar (1.5 cm<sup>3</sup>/min).

Alcohols, acetates, and ketones were analysed on a glass capillary column (47 m × 0.3 mm i. d.) coated with phenyldiethanolamine succinate (PDEAS) at 150°C, sampler 260°C, carrier gas Ar (1.5 cm<sup>3</sup>/min).

**NMR <sup>13</sup>C spectra,** WH-90 and AM-50 spectrometers, frequency <sup>13</sup>C 22.63 MHz and 125.76 MHz in the solution of CDCl<sub>2</sub>, inner standard — TMS.

**Acknowledgements.** The authors are grateful to Mr. T. Välimäe for taking NMR <sup>13</sup>C spectra and to Mrs. M. A. Somova and coworkers for determining organoleptically the fragrant characteristics of compounds at the Laboratory of Perfumery, Severnoye Siyanie Perfumery Plant, St. Petersburg.

#### REFERENCES

1. *Baeyer, A., Perkin, W. H.* Berichte der Deutschen Chemischen Gesellschaft, 1866, **16**, 187. Cited in Beilstein H, Bd. VII, 373.
2. *Arctander, S.* Perfume and Flavour Chemicals, 1969, Vol. I, No. 318.
3. *Arctander, S.* Perfume and Flavour Chemicals, 1969, Vol. II, No. 2171.
4. *Arctander, S.* Perfume and Flavour Chemicals, 1969, Vol. II, No. 2609.
5. *Бибичева А. И., Андреев В. М.* Душистые вещества из продуктов алкилирования кетонов пренилхлоридом. I. 2-Метил-6-фенил-2-гексен-6-он и продукты его гидрирования. — Ж. орг. хим., 1972, **8**, 1389—1392; *Андреев В. М., Бибичева А. И., Журавлева М. Н.* Душистые вещества из продуктов алкилирования кетонов пренилхлоридом. II. Алкилирование кетонов по методу Манкоши. — Ж. орг. хим., 1974, **10**, 1470—1473.
6. *Sprecher, M. A.* IFF. US Patent No. 4507225. 1985.

7. *Fuson, Ross, McKeever*. J. Amer. Chem. Soc., 1939, **61**, 414. Cited in Beilstein E III, Bd. VII, 1495.
8. *Darzens, G.* Compt. Rend. Acad. Sc., 1940, **211**, 435. Cited in Beilstein E III, Bd. VII, 1492—1495.
9. *Челнзев В. В., Патарая А. В.* Кетоны и непредельные кетоны. — Ж. общ. хим., 1941, **11**, 5—6, 461—465.
10. *Лээтс К. В., Чернышев В. О., Ранг Х. А.* Способ получения ароматических кетонов. Авт. свид. СССР № 574434 от 30. 09. 1977. — Б. И., 1977, **36**, 62.
11. *Чернышев В. О., Ранг Х. А., Лээтс К. В.* 3-Метил-1-фенил-4-гексен-1-оны в качестве душистых веществ. Авт. свид. СССР № 721402 от 15. 03. 1980. — Б. И., 1980, **10**, 92.
12. UK Patent 2 163 148, 23. 04. 1987.
13. *Пехк Т., Чернышев В., Вялимяе Т., Ранг Х., Лээтс К.* Применение спектроскопии ЯМР <sup>13</sup>C для определения структуры и конфигурации диастереоизомеров в ароматических продуктах реакции теломеризации. — Изв. АН ЭССР. Хим., 1982, **31**, 4, 258—262.
14. *Ранг Х. А., Чернышев В. О., Эрм А. Ю., Пехк Т. И., Лээтс К. В.* 3-Метил-1-фенил- (или метилфенил)-4-гексенолы и их ацетаты в качестве душистых веществ. Авт. свид. СССР № 685658 от 15. 09. 1979. — Б. И., 1979, **34**, 149.
15. *Лээтс К. В., Ранг Х. А., Чернышев В. О., Вийтмаа С. О.* 5-Метил-(3'-метилфенил)-4-гексен-1-ол в качестве компонента для парфюмерных композиций. Авт. свид. СССР № 1008207 от 30. 03. 1983. — Б. И., 1983, **12**, 130.
16. *Лээтс К. В., Чернышев В. О., Ранг Х. А., Вийтмаа С. О.* Ацетат 5-метил-1-метилфенил-4-гексен-1-ола в качестве компонента душистой композиции. Авт. свид. СССР № 979330 от 07. 12. 1982. — Б. И., 1982, **45**, 98.

Received  
March 9, 1992

*Heino RANG, Sirje VIITMAA, Koit LÄÄTS*

### 1-FENÜÜLDIMETÜÜLHEKSEENI 1-OKSI- JA 1-OKSODERIVAATIDE SUNTEES NING NENDE LÖHNNA KARAKTERISTIKA

On sünteesitud 1-fenüül (ja metüülfenüül)-3,5-dimetüülhekseeni 1-kloro-, 1-oksi- ja 1-oksoderivaadid. Neist okso- ja oksiühendid ning nende atsetaadid on lõhnaained. On näidatud, et alkenüülahela metüülrühmad asendis 3 ja 5 suurendavad lõhna intensiivsust ja püsivust.

*Хейно РАНГ, Сирье ВИИТМАА, Коит ЛЭЭТС*

### СИНТЕЗ 1-ОКСИ- И 1-ОКСОПРОИЗВОДНЫХ 1-ФЕНИЛДИМЕТИЛГЕКСЕНА И ИХ ДУШИСТЫЕ ХАРАКТЕРИСТИКИ

Синтезированы 1-хлоро-, 1-окси- и 1-оксопроизводные 1-фенил(и метилфенил)-3,5-диметил-4-гексена. Из них оксо-, оксипроизводные и их ацетаты являются душистыми веществами. Показано, что метильные группы в положениях 3 и 5 увеличивают интенсивность и стойкость запаха.