March 16, 1965 M. G. J. BEETS ETAL 3,173,955

ARYL-ALKENONES

Filed Aug. 1, 1962 2 Sheets-Sheet 1

FIG. 1

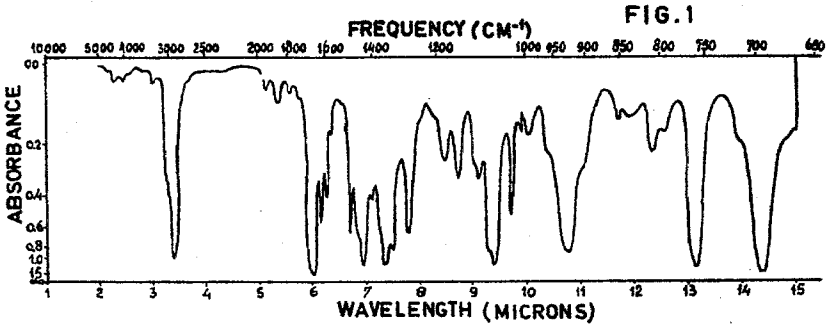


FIG. 2

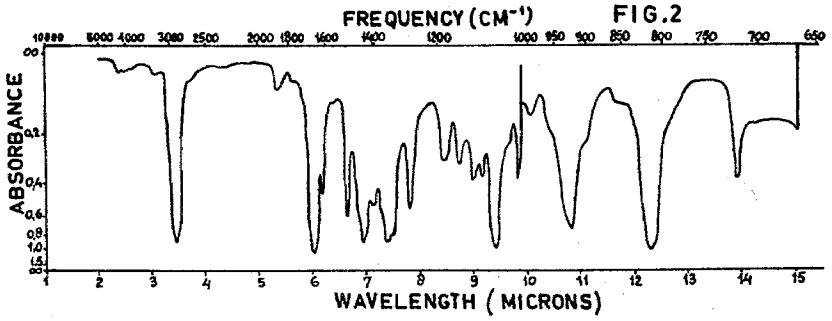


FIG. 3

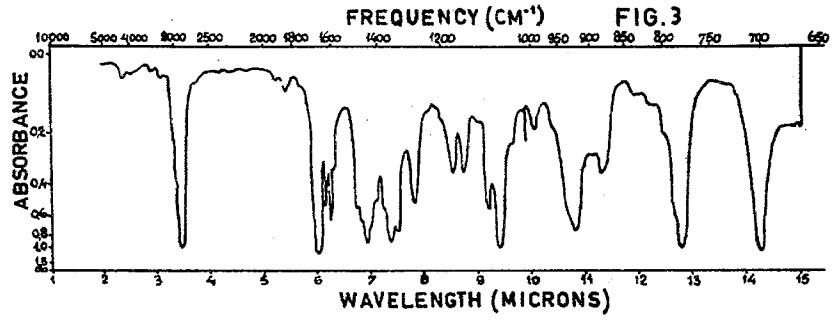
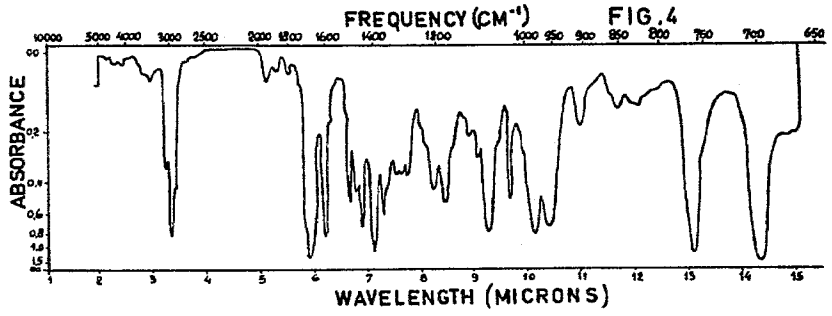


FIG. 4



INVENTORS
MOUS G. J. BEETS
WILHELMINA MEERBURG
WILHELMUS J. WIEGERS
BY
Ward, Neal, Haselton, Orme & McElhannon

March 16, 1965 M. G. J. BEETS ETAL 3,173,955

ARYL-ALKENONES

Filed Aug. 1, 1962 2 Sheets-Sheet 2

FIG.5

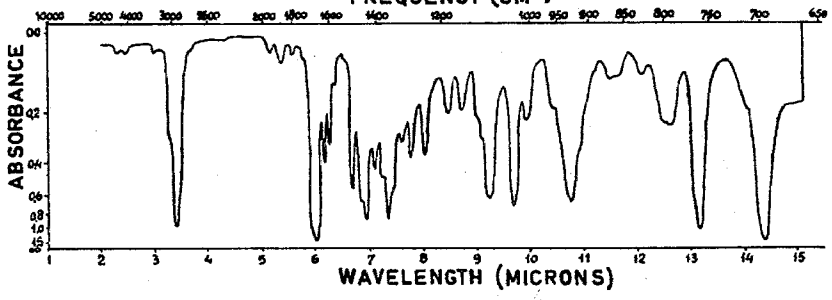


FIG.6

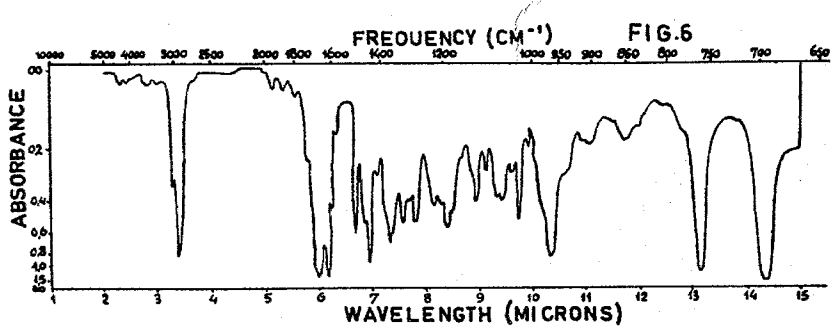
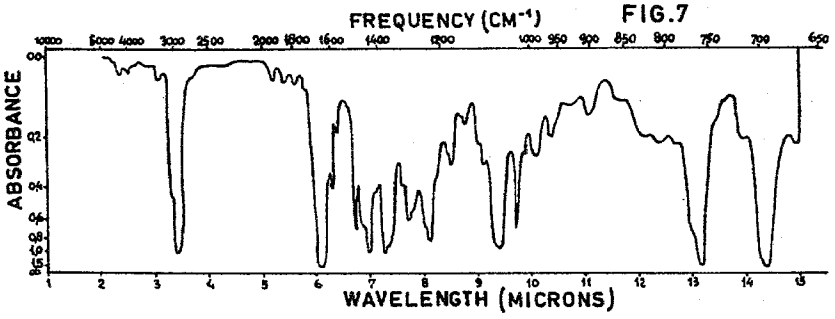


FIG.7



INVENTORS
MOUS G.J. BEETS
WILHELMINA MEERBURG
BY WILHELMUS J. WIEGERS
Ward, Neal, Haselton, Orme & McElhannon

United States Patent Office

3,173,955
Patented Mar. 16, 1965

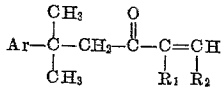
3,173,955

ARYL-ALKENONES

Muus G. J. Beets, Wilhelmina Meerburg, and Wilhelmus J. Wiegers, Hilversum, Netherlands, assignors to International Flavors & Fragrances I.F.F. (Nederland) N.V., Zaandam, Provincialeweg, Netherlands

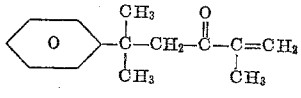
Filed Aug. 1, 1962, Ser. No. 214,063
Claims priority, application Great Britain, Aug. 9, 1961, 28,740/61
7 Claims. (Cl. 260—590)

We have discovered that unsaturated aryl aliphatic ketones of the general structure I in which Ar is phenyl or methylphenyl and in which R_1 and R_2 are hydrogen or lower alkyl with a total number of carbon atoms not exceeding two, are outstanding perfumes.



(I)

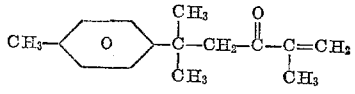
Especially in the case where Ar is phenyl, R_1 is methyl and R_2 is hydrogen, the compound (II) represents a new material of extraordinary intensive and valuable odour.



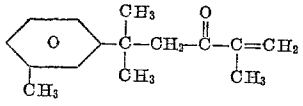
(II)

Although 2,5-dimethyl-5-phenyl-hexen-1-one-3 (II) has a strong interesting and definite odour, it is easy to blend into specific and widely varying types of perfumes in relatively large amounts. It shows an excellent tenacity and can be used in perfume composition as well as in articles in which such compositions are used such as soaps, cosmetics, powders, aerosols, creams, lotions and the like.

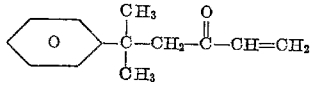
The same holds good for other representatives of this group of which the compounds III–VIII, all with excellent properties, are mentioned as examples.



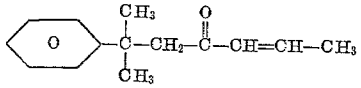
(III)



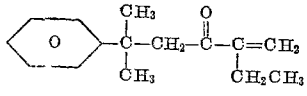
(IV)



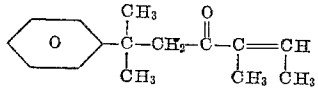
(V)



(VI)



(VII)



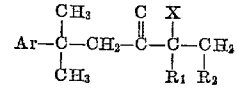
(VIII)

We have also discovered that compounds according to this invention are useful as flavouring materials.

Products according to the present invention may be obtained in several ways of which the following are mentioned as examples.

(A) Elimination of HX from compounds of the general type IX, in which Ar, R_1 and R_2 have the meaning

mentioned above and in which X can represent hydroxyl, halogen or an ester group.

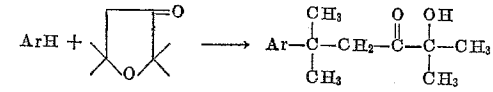


(IX)

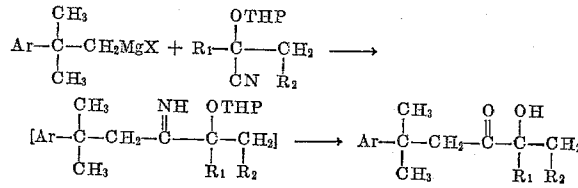
This can be realized either by direct dehydration of the carbinol (X=OH) under the influence of catalysts such as sulphuric acid, toluene sulphonic acid, acid salts, boric anhydride, boric acid or by pyrolysis of the corresponding esters such as acetates, propionates, stearates, metaborates, xanthates or sulphites.

Compounds of type IX may be obtained in several ways of which the following examples are mentioned.

(1) Friedel Crafts condensation of aromatic hydrocarbons with tetra alkyl tetrahydrofuranone (see H. A. Bruson, J.A.C.S. 80, 3636 (1958))

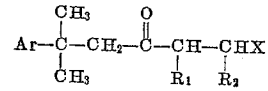


(2) Condensation of neophylmagnesiumhalides with cyanohydrins of ketones or aldehydes in which the hydroxyl group is protected, e.g. by means of a tetrahydropyranyl group



where OTHP is a tetrahydropyranyl group.

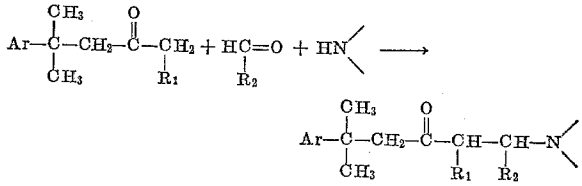
(B) Elimination of HX from compounds of the general type X, in which Ar, R_1 and R_2 have the meaning mentioned above and in which X can represent hydroxyl, halogen, an ester group or a tertiary amino group



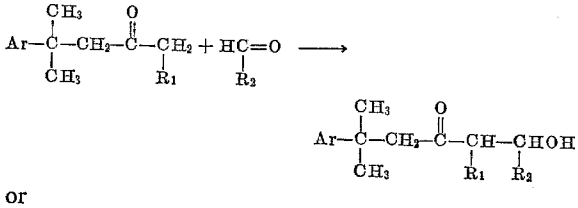
(X)

This can be carried out either by pyrolysis or by elimination under the influence of alkali or acid. Compounds of type X may be obtained in several ways of which the following examples are mentioned.

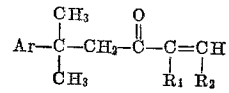
(1) Mannich reaction of ketones with aldehydes and amines



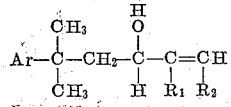
(2) Aldol condensation of ketones with aldehydes.



or

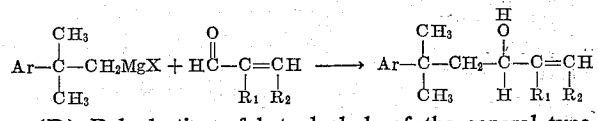


(C) Oxidation or catalytic dehydrogenation of unsaturated alcohols of type XI in which Ar, R_1 and R_2 have the meaning, mentioned above.

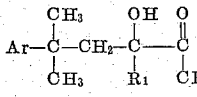


(XI)

This can be carried out by several known methods, e.g. with chromic acid, with manganese dioxide etc. Alcohols of type XI are easily accessible by condensation of neophylmagnesium halides and unsaturated aldehydes.

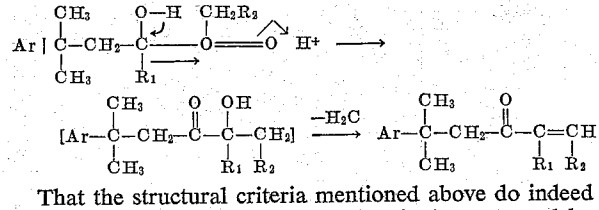


(D) Dehydration of ketoalcohols of the general type XII under conditions which favour rearrangement



(XII)

When a carbinol of type XII is dehydrated catalytically in the presence of acid a rearrangement takes place which may be formulated as follows



That the structural criteria mentioned above do indeed delimitate the scope of the invention is demonstrated by the following considerations.

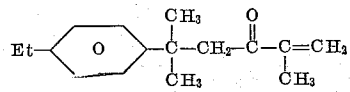
(1st) The introduction of a methyl group in the aromatic nucleus causes a slight decrease in the intensity of the odour but the compounds III and IV still retain the powerful rose-type odour of II, although shifted somewhat towards the woody type.

When, however, an ethyl group is introduced into the phenyl group, the odour weakens considerably. XIII (B.P.$_{3\ mm.}$ 122°; n_D^{20} 1.5158) as well as XIV (B.P.$_{3\ mm.}$ 119°; n_D^{20} 1.5151) have a characteristic but rather weak odour.

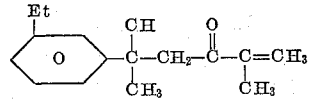
(2nd) Replacement of one of the gemini methyl groups by ethyl XV (B.P.$_{3\ mm.}$ 116°; n_D^{20} 1.5170) leads to a considerable decrease of the odour.

(3d) The compound XVI (B.P.$_{3\ mm.}$ 130°; n_D^{20} 1.5157), obtained by aldol condensation of isobutyric aldehyde with 2-methyl-2-phenyl-pentanone-4 has a very weak odour.

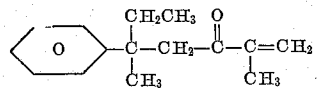
(4th) 2,5 - dimethyl - 2 - phenyl - hexanone - 4 (XVII; B.P.$_{3\ mm.}$ 100°; n_D^{20} 1.5001; d_4^{20} 0.9496), obtained by hydrogenation of II, possesses a fairly weak, uncharacteristic odour.



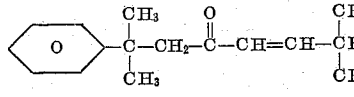
(XIII)



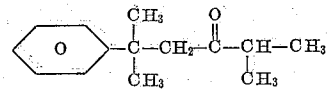
(XIV)



(XV)



(XVI)



(XVII)

The following examples may illustrate the preparation of compounds according to the present invention.

(1) *2,5-dimethyl-5-phenyl-hexene-1-one-3*

106 g. (0.40 mole) of 2-acetoxy-2,5-dimethyl-5-phenyl-hexanone-3 (B.P.$_{3\ mm.}$ 134°; n_D^{20} 1.4993) were introduced at a pressure of 100 to 110 mm. (nitrogen atmosphere) into a reactor consisting of a glass tube packed with glass helices at 350° to 400° C. during 4 hours. The crude reaction product was washed to neutral reaction and fractionated through a 16-plate Vigreux column. The yield was 75 to 80%. All fractions showed a constant boiling point and refractive index and were pure on gas chromatography. n_D^{20} 1.5222; B.P.$_{3\ mm.}$ 110° C.; colourless liquid.

The product is stabilized with a small amount of one of the usual inhibitors such as hydroquinone. In unstabilized form it shows a tendency to dimerize. However, upon heating (distillation) the dimer dissociates easily and the monomer can always be recovered in nearly quantitative yield.

Melting point semicarbazone: 156.4–157.0°. The infrared spectrum is shown in FIGURE 1 of the accompanying drawing.

(2) *2,5-dimethyl-5(4'-methylphenyl)-hexene-1-one-3 and 2,5-dimethyl-5(3'-methylphenyl)-hexene-1-one-3*

2,5 - dimethyl - 5 - (methyl - phenyl) - hexanol - 2-one-3 (B.P.$_{3\ mm.}$ 132°; n_D^{20} 1.5092–1.5098; mixture of m- and p-isomers) was obtained by condensation of toluene with tetramethyl-tetrahydrofuranone according to Bruson.

The corresponding acetate (B.P.$_{3\ mm.}$ 145°; n_D^{20} 1.4992) was pyrolyzed according to Example 1.

A mixture of about 72% para and 28% meta-isomers of the desired product (B.P.$_{3\ mm.}$ 115°; n_D^{20} 1.5200; d_4^{20} 0.9705) was obtained in 70% yield. Colourless liquid with strong odour, the rose character of which is shifted somewhat towards the woody note. The two isomers could be separated by gas liquid partition chromatography (G.L.P.C.). 2,5-dimethyl-5-(4'-methyl-phenyl)-hexene-1-one-3; n_D^{20} 1.5196 p-isomer; corresponding m-isomer; n_D^{20} 1.5202. The I.R. spectra of these compounds are shown in FIGURES 2 and 3.

(3) *2,5-dimethyl-5-phenyl-hexene-1-one-3*

In a 250 ml. distillation flask, fitted for continuous azeotropic water separation were placed 55 g. of xylene, 5.5 g. of toluene-sulphonic acid and 55 g. (0.25 mole) of 2,5-dimethyl-5-phenyl-hexanol-2-one-3 (B.P.$_{3\ mm.}$ 125°; n_D^{20} 1.5100). The solution was refluxed for 30 min. during which period nearly the theoretical amount of water was separated. The xylene solution was washed and fractionated. B.P.$_{2,5\ mm.}$ 103°; n_D^{20} 1.5220. The product contained only traces of 1,1,4,4-tetramethyl-tetralone (M.P. 74.8–75.3°).

(4) *2,5-dimethyl-5-phenyl-hexene-1-one-3*

110 g. (0.5 mole) of 2,5-dimethyl-5-phenyl-hexanol-2-one-3 were introduced into a reactor consisting of a glass-tube packed with 17.5 g. of boric anhydide on 45.5 g. of pumice in nitrogen atmosphere at 100—110 mm. and at 260° C. in 2½ hours. Since the conversion was incomplete (checked by G.L.P.C.) the treatment was repeated twice until the G.L.P.C. analysis of the crude product showed the absence of starting material.

The crude reaction product was washed and fractionated through a 16-plate Vigreux column. The yield was 65% of theory. n_D^{20} 1.5220–1.5223. B.P.$_{2.5\ mm.}$ 105–107° C.

(5) *2,5-dimethyl-5-phenyl-hexene-1-one-3*

110 g. (0.5 mole) of 2,5-dimethyl-5-phenyl-hexanol-2-one-3 were heated with 34.5 g. (0.55 mole) of boric acid and 0.11 g. hydroquinone to 140° at 15 mm. while water was removed by distillation and kept at 140° for 45 minutes. The reaction product was flash distilled and fractionated in vacuo. 37% of theory of the desired product were obtained while 34% of starting material was recovered.

(6) *2,5-dimethyl-5-phenyl-hexene-1-one-3*

25 g. (0.114 mole) of 2,5-dimethyl-5-phenyl-hexanol-2-one-3 were slowly distilled in the presence of 4.4 g. (0.063 mole) of boric anhydride through a 16-plate Vigreux column at 13.5 mm. The reaction product was refractionated and 2,5-dimethyl-5-phenyl-hexene-1-one-3 ($B.P._{1.5\ mm.}$ 100.5°; n_D^{20} 1.5219–1.5221) was obtained in a yield of 58%.

(7) *5-methyl-2-ethyl-5-phenyl-hexene-1-one-3 and 2,5-dimethyl-2-phenyl-heptene-5-one-4*

To a solution of 4 g. of gaseous hydrochloric acid in 400 g. of ether was added in 1 hour at 25–30° a mixture of 840 g. (10 moles) of dihydropyran and 792 g. (8.0 moles) of 2-cyano-butanol-2 ($B.P._{3\ mm.}$ 62°; n_D^{20} 1.4140). A solution of 2 g. of gaseous hydrochloric acid in 200 g. of ether was added and the mixture was allowed to stand overnight. The reaction product was stirred with a solution of 400 g. of potassium carbonate in 600 g. of water, worked up and fractionated in vacuo. Yield of 2-tetrahydropyranyloxy-2-cyanobutane 83% of the theory. $B.P._{3\ mm.}$ 78°, n_D^{20} 1.4432–1.4456.

A solution of neophylmagnesiumchloride was prepared from 228.4 g. (9.4 moles) of magnesium in 860 g. of dry ethyl-butylether and from 1516.5 g. (9.0 moles) of neophylchloride in 1516 g. of ethylbutylether in the usual way.

At 35–45° a solution of 1134.6 g. (6.2 moles) of the tetrahydropyranylether obtained in the same amount of ethylbutylether was added in 1½ hours.

Stirring was continued at reflux temperature for 2 hours and 3000 g. of water were added at reflux temperature in 1 hour. 2160 g. (36 moles) of acetic acid and 1300 ml. of 36% hydrochloric acid were added. After the addition of each the mixture was stirred for 1 hour at 40–50°.

After having been worked up, the crude product was fractionated through a 16-plate Vigreux column.

The 2,5-dimethyl-2-phenyl-heptanol-5-one-4 obtained ($B.P._{3\ mm.}$ 132°; n_D^{20} 1.5078; pure on G.L.P.C., crystallizes on standing) was converted into the acetic acid ester ($B.P._{3\ mm.}$ 145°; n_D^{20} 1.4998, ester value 202.2 or 99.6%) in the usual way. Yield 96%.

The pyrolysis was carried out according to Example 1 at 450–470° at 190 mm. in nitrogen atmosphere. A mixture of two isomers was obtained in a ratio of 3:2 which could be separated by fractionation at 3 mm. through a 16-plate Vigreux column.

(*a*) 5-methyl-2-ethyl-5-phenyl-hexene-1-one-3; $B.P._{3\ mm.}$ 119°; n_D^{20} 1.5182; d_4^{20} 0.9694; I.R. spectrum FIG. 5.
(*b*) 2,5-dimethyl-2-phenyl-heptene-5-one-4; $B.P._{3\ mm.}$ 125°; n_D^{20} 1.5280; d_4^{20} 0.9785; I. R. spectrum FIG. 7.

The odour of the first mentioned compound has a strong rose-like character, shaded to a green, rue like quality, that of the latter is similar, but more green and twiggy.

(8) *2-methyl-2-phenyl-hexen-5-one-4*

2-tetrahydropyranyloxy-propionitrile ($B.P._{3\ mm.}$ 70°; n_D^{20} 1.4397–1.4450; mixture of diastereomers according to G.L.P.C.) was condensed with neophyl magnesiumchloride according to Example 7. The hydroxyketone (2 components on G.L.P.C.) was converted into the acetate which was pyrolyzed according to Example 1. The product of the pyrolysis contained about 25% of recovered acetate, about 10% of 2-methyl-2-phenyl-hexene-5-one-4 ($B.P._{3\ mm.}$ 103°; n_D^{20} 1.5251; I.R. spectrum FIG. 4) and 33% of 2-methyl-2-phenyl-hexene-3-one-5 ($B.P._{3\ mm.}$ 114°; n_D^{20} 1.5348).

(9) *2-methyl-2-phenyl-heptene-5-one-4*

2-tetrahydropyranyloxybutyronitrile, ($B.P._{3\ mm.}$ 83°; n_D^{20} 1.4428–1.4451, mixture of 2 steroisomers according to G.L.P.C.) was condensed according to Example 7 with neophylmagnesiumchloride. The hydroxyketone obtained was converted into the acetate which was pyrolyzed according to Example 1. 2-methyl-2-phenyl-hepten-5-one-4 was obtained as a colourless liquid with an intensive odour ($B.P._{3\ mm.}$ 116°, n_D^{20} 1.5270).

(10) *2-methyl-2-phenyl-hexene-5-one-4*

880 g. (5.0 moles) of 2-methyl-2-phenyl-pentanone-4, 478.5 g. (5.5 moles) of morpholine, 1250 ml. of isopropanol, 573 g. (5.5 moles) of 35% hydrochloric acid and 217.5 g. (7.25 moles) of para formaldehyde were refluxed for 12 hours. The reaction product was diluted with 3000 g. of water, the neutral parts, 58 g., were extracted with benzene and 600 g. of 25% ammoniumhydroxide solution was added to the aqueous solution. The aminoketone (1313 g., n_D^{20} 1.5233) was extracted with benzene and converted into the hydrochloric acid salt with an ethereal solution of hydrochloric acid. Melting point, after recrystallisation from acetone 123.2–124.0°.

290 g. (0.93 mole) of the so obtained Mannich salt were heated at 3 mm. Decomposition started at 130°. The crude distillate was dissolved in benzene, washed and fractionated through a 16-plate Vigreux column. 2-methyl-2-phenyl-hexene-5-one-4 was obtained as a colourless liquid with an odour of the type of geranyl- and citronellyl-esters. $B.P._{0.2\ mm.}$ 68°; n_D^{20} 1.5250, d_4^{20} 0.9873. With phenylhydrazine a pyrazolin derivative of M.P. 85.0–85.5° was obtained. A part from the desired product some 2-methyl-2-phenyl-pentanone, formed by retro Mannich reaction was obtained.

The product was shown to be identical to that obtained according to the method described in Example 8.

(11) *5-methyl-2-ethyl-5-phenyl-hexene-1-one-3*

2-methyl-2-phenyl-heptanone-4 was converted into the Mannich salt according to Example 10. After decomposition according to the same example the reaction product was fractionated through a 17-plate Vigreux column.

5 - methyl-2-ethyl-5-phenyl-hexene-1-one-3 ($B.P._{3\ mm.}$ 15°; n_D^{20} 1.5180; d_4^{20} 0.9690) was obtained as a colourless liquid with a powerful odour of the rose type which has shifted towards green rue-like notes.

The product was shown to be identical with the compound obtained according to Example 7.

(12) *2,5-dimethyl-5-phenyl-hexene-1-one-3*

Neophylmagnesiumchloride, prepared in ethyl-butylether, was condensed with methacrolein at 0–10°. The reaction-product was fractionated through a saddle column of 25 cm. at 3 mm. Yield of 2,5-dimethyl-5-phenyl-hexene-1-ol-3 60%; $B.P._{3\ mm.}$ 115°; n_D^{20} 1.5208, d_4^{20} 0.9675. Some 2,5-dimethyl-5-phenyl-hexanal (formed by 1,4 addition) was obtained as a byproduct.

51 g. (0.25 mole) of the pure unsaturated alcohol, 87 g. (1.0 mole) of manganese dioxide and 500 ml. of benzene were refluxed for 10 hours. 3.0 ml. of water were removed azeotropically during this period. Excess manganesedioxide was removed and washed and the reaction product was distilled. Weight: 42 g. G.L.P.C. showed that it consists of 80% of the desired ketone and 20% of unconverted alcohol. Fractionation in vacuo yielded pure 2,5 - dimethyl-5-phenyl-hexene-1-one-3, $B.P._{3\ mm.}$ 106°, n_D^{20} 1.5221.

(13) *2-methyl-2-phenyl-heptene-5-one-4*

Neophylmagnesiumchloride was condensed in ethylbutylether with crotonic aldehyde. 2-methyl-2-phenylheptene-5-ol-4 was obtained in a yield of 60%. B.P.$_{.3\ mm.}$ 116°; n_D^{20} 1.5201; d_4^{20} 0.9620. To a solution of 448.5 g. (2.2 moles) of the unsaturated alcohol obtained in 1100 ml. of acetone, a solution of 440 g. (1.48 moles) of sodiumbichromate 2 aq. and 580 g. (5.68 moles) of concentrated sulphuric acid in 2200 ml. of water were added in 2 hours at 0–5° C.

Stirring was continued for 1 hour at 5–10° and the reaction product was worked up.

387 g. of distillate (B.P.$_{.3\ mm.}$ 110–160°; n_D^{20} 1.5251), containing 81.4% of ketone were obtained and subjected to a boric ester separation. The ketone obtained was fractionated at 3 mm. through a 16-plate Vigreux column. Two products were obtained; 2-methyl-2-phenyl-heptene-5-one-4 (main product; B.P.$_{.3\ mm.}$ 15–118°; n_D^{20} 1.5268–1.5272, assay by oximation 99%) and 2-methyl-2-phenyl-heptene-4-one-6 (by rearrangement; B.P.$_{.3\ mm.}$ 124°; n_D^{20} 1.5280; d_4^{20} 0.9731). The odour of the latter compound is far less interesting than that of the main product.

2-methyl-2-phenyl-heptene-5-one-4 is a colourless liquid with strong odour reminescent of jasmin absolute and of rhum. The I.R. spectrum is shown in FIG. 6.

(14) *2-methyl-2-(methyl-phenyl)-heptene-5-one-4*

Methyl-neophylmagnesiumchloride was condensed with crotonic aldehyde and the unsaturated alcohol obtained was oxidizde, according to Example 13.

The desired ketone was obtained as a colourless liquid; B.P.$_{0.6\ mm.}$ 104–110°; n_D^{20} 1.5250–1.5260. The odour is suggestive of jasmin.

2-methyl-2-methylphenyl-heptene-4-one-6 (B.P.$_{0.6\ mm.}$ 110–116°; n_D^{20} 1.5260–1.5270; formed by rearrangement) was obtained as a byproduct. The odour is weak with a touch of cedarwood.

(15) *2,5-dimethyl-5-phenyl-hexene-1-one-3*

50.5 g. (0.23 mole) of 2,4-dimethyl-2-phenyl-hexanol-4-one-5 (B.P.$_{0.4\ mm.}$ 92° C.; n_D^{20} 1.5148) and 8.9 g. (0.127 mole) of boric anhydride were placed in a distillation flask fitted with a 16-plate Vigreux column and fractionated slowly at 13 mm., the reflux ratio and the boil-up rate being selected in such a way that practically only the desired product and no starting material was obtained in the receiver. The reflux ratio was reduced gradually from 1/60 to 1/5 in such a way that the refractive index was maintained at 1.521–1.522 (i.e. the refractive index of the desired material). The distillate was fractionated through a 16-plate Vigreux column in the presence of 0.03 g. of hydroquinone and 0.03 of copper powder. The yield was 50% of theory. B.P.$_{1.5\ mm.}$ 97°, n_D^{20} 1.5220–1.5222.

Finally, a number of simple formulae are given which illustrate the application of some of the new compounds disclosed by this invention.

(1) *Rose-type composition*

40 parts phenyl ethyl alcohol
15 parts geraniol ex citronella oil
15 parts citronellol
20 parts 2,5-dimethyl-5-phenyl-hexen-1-one-3
5 parts α-ionone
5 parts hydroxy-dihydrocitronellal

100 parts

Replacement of 2,5-dimethyl-5-phenyl-hexen-1-one-3 by rhodinol gives a considerably lower odour quality.

(2) *Jasmin-type composition*

33 parts benzyl acetate
5 parts linalool
10 parts 2,5-dimethyl-5-phenyl-hexen-1-one-3
2 parts methyl-ionone
10 parts hydroxy-dihydrocitronellal
13 parts phenyl ethyl alcohol
25 parts α-amylcinnamic aldehyde
2 parts oil of ylang-ylang

100 parts

(3) *Violet-leaftype composition*

40 parts γ methylionone
15 parts β ionone
2 parts heliotropin
5 parts oakmoss resoin 10% in benzyl-benzoate
3 parts benzylacetate
5 parts orris concrete 10% in benzyl-benzoate
10 parts methyl heptin carbonate 10% in benzyl-benzoate
5 parts phenyl ethyl alcohol
15 parts 5-methyl-2-ethyl-5-phenyl-hexene-1-one 3

100 parts

A comparison between the composition before and after the addition of the compound according to the invention shows that the latter smoothes the odour and gives it a true violetleaf effect. This effect is still stronger after 20 hours on the smelling strip.

(4) *Jasmin-type composition*

25 parts of benzylacetate
5 parts of benzylpropionate
5 parts of linalool
5 parts of linalylacetate
5 parts of hydroxydihydrocitronellal
20 parts of α-amylcinnamic aldehyde
10 parts of phenyl ethyl alcohol
2 parts of ylang ylang oil
3 parts of heliotropin
20 parts of 2-methyl-2-phenyl-heptene-5-one-4

100 parts

Comparison of the composition before and after addition of the compound according to the invention shows that the latter imparts to the composition a smooth, sweet jasmin effect.

After 20 hours on the smelling strip the first mentioned composition has a rough odour whereas the latter shows a natural jasmin character.

(5) *Neroli-type composition*

25 parts of terpeneless petitgrain oil
5 parts of linalool
10 parts of linalyl acetate
1 part of methyl anthranilate
5 parts of geraniol
10 parts of phenyl ethyl alcohol
10 parts of terpeneless bergamotte oil
2 parts of bitter orange oil
2 parts of methyl-β-naphthylketone
30 parts of 2,5-dimethyl-2-phenyl-heptene-5-one-4

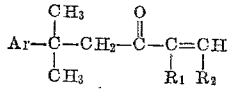
100 parts

The addition of the compound according to the invention has an extremely favourable effect, especially on the backnote of the composition.

All temperatures herein referred to are in ° C.

What we claim is:

1. An aryl-alkenone having the formula



in which Ar is selected from the group consisting of phenyl and 3' and 4' methylphenyl, and in which R_1 and R_2 are selected from the group consisting of hydrogen, methyl and ethyl, the total number of carbon atoms in R_1 and R_2 not exceeding 2.

2. 2,5-dimethyl-5-phenyl-hexene-1-one-3.
3. 2,5-dimethyl-5-(3'-methyl-phenyl)-hexen-1-one-3.
4. 2,5-dimethyl-5-(4' methyl-phenyl)-hexen-1-one-3.
5. 5-methyl-2-ethyl-5-phenyl-hexene-1-one-3.
6. 2,5-dimethyl-2-phenyl-heptene-5-one-4.
7. An aryl-alkenone 2-methyl-2-phenyl-heptene-5-one-4.

References Cited in the file of this patent

Rupe et al.: Helv. Chim. Acta, vol. 17, pages 372–89 (1934) (page 376 relied upon).

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,173,955 March 16, 1965

Muus G. J. Beets et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 32, for "composition" read -- compositions --; column 3, lines 26 to 33, for that portion of the formula reading:

$\xrightarrow{-H_2C}$ read $\xrightarrow{-H_2O}$

column 6, line 51, for "15°" read -- 115° --; column 7, line 19, for "15-118°" read -- 115-118° --; same column 7, line 33, for "oxidizde" read -- oxidized --.

Signed and sealed this 3rd day of August 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents