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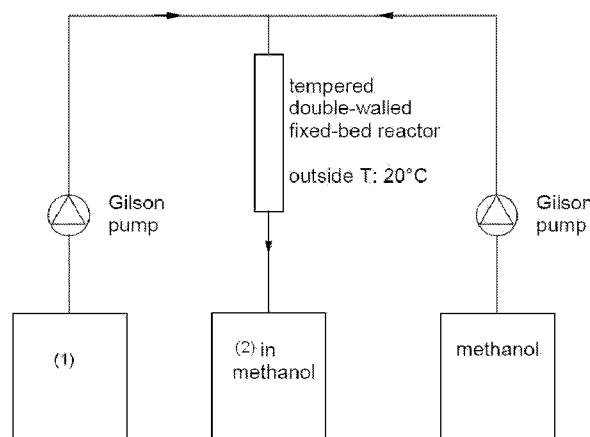
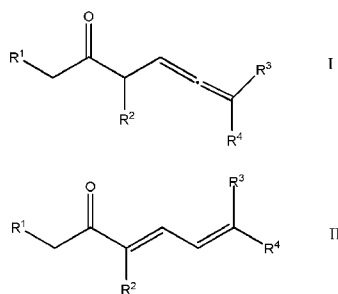
(54) Title: ISOMERIZATION OF β -KETO-ALLENES

Fig. 1

(57) Abstract: Isomerization of β -keto-allenes of the general formula I wherein R^1 is hydrogen, methyl or ethyl, in particular hydrogen or methyl; R^2 is hydrogen or methyl; R^3 is hydrogen or methyl, in particular methyl and R^4 is an aliphatic hydrocarbon residue containing 1 - 37 carbon atoms, into corresponding α,γ -dienones of formula II by treatment with a basic ion exchange resin.



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Isomerization of β -keto-allenes

The present invention relates to the isomerization of β -keto-allenes. More specifically,
5 the present invention relates to the isomerization of β -keto-allenes to α,γ -dienones under catalysis of basic ion exchange resins.

α,γ -Dienones are interesting compounds for the flavour and fragrance industry and valuable intermediates in the synthesis of carotenoids and vitamins A (Carotenoids, ed. O.
10 Isler, Birkhäuser Verlag Basel und Stuttgart, 1971). The preparation of α,γ -dienones from β -keto-allenes is known in the art.

Saucy et al. (Helv. Chimica Acta 50, 1158-1167 [1967]) have described the preparation of β -keto-allenes and their isomerization into conjugated dienones (α,γ -dienones) in an
15 exothermic reaction in the presence of alcoholic alkali in petroleum ether (two-phase system) at 10 °C. Thus, e.g., 6-methyl-3,5-heptadien-2-one, pseudoione and pseudoiron were obtained.

WO 2008/092655 A1 discloses the isomerization of β -keto-allenes to α,γ -dienones with
20 aqueous sodium hydroxide in methanol under temperature control with dry-ice/alcohol bath because of the strongly exothermic reaction.

EP 0 418 690 discloses the isomerization of 8-(2'2'-dimethylcyclopropyl)-6-methyl-4,5-octadien-2-one in an organic solvent with a strong organic or mineral acid or with a
25 strong aqueous base (30 % - 50 % NaOH or KOH) in an alcohol (methanol or ethanol) at

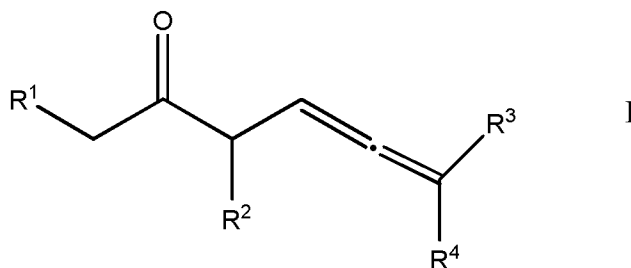
0 °C - 10 °C (see, e.g., Saucy et al., *supra*). The use of acidic ion exchange resins, e.g., Amberlite IR 120, etc., has also been mentioned, however, without exemplification.

EP 0 647 624 describes the isomerization of the C₁₈-β-keto-allene 8-(1,1,5-trimethyl-cyclo-4-hexenyliden)-6-methyl-octa-4,5-dien-2-one into 8-(1,1,5-trimethyl-cyclo-5-hexenyl)-6-methyl-3,5,7-trien-2-one (a C₁₈-intermediate in the synthesis of vitamin A) by treatment with hydrobromic acid in acetone under cooling to about 0 °C. By treatment of the C₁₈-β-keto-allene in methylene chloride with diazabicycloundecene or in methanol with sodium carbonate 8-(1,1,5-trimethyl-cyclo-4-hexenyliden)-6-methyl-3,5-octadien-2-one is obtained.

According to Ullmann's Encyclopedia of Industrial Chemistry, 5th, completely revised edition, Vol. A5, 1986, p. 344, the catalytic activity of organic ion exchangers can be used advantageously in many important industrial reactions. Isomerization reactions are not among those which have been mentioned specifically let alone the isomerization of β-keto-allenes into α,γ-dienones.

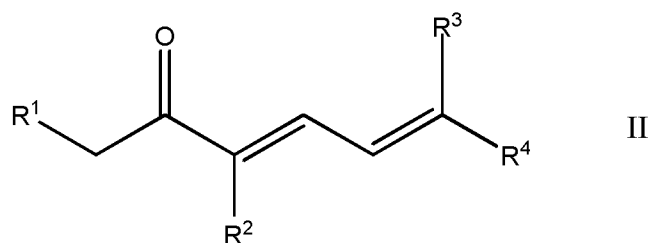
Starting from the task of developing commercially attractive methods of isomerization of β-keto-allenes into α,γ-dienones which can be conducted preferably continuously and avoid the use of acidic or basic solvents which have to be neutralized during work-ups it has been found that basic ion exchange resins can be used advantageously as catalysts in this isomerization.

The present invention, therefore, relates to the isomerization of β-keto-allenes of the general formula



wherein R¹ is hydrogen, methyl or ethyl, in particular hydrogen or methyl;
R² is hydrogen or methyl;
R³ is hydrogen or methyl, in particular methyl and
R⁴ is an aliphatic hydrocarbon residue containing 1 – 37 carbon atoms,

into corresponding α,γ -dienones of formula



by treatment with a basic ion exchange resin, preferably a strongly basic, macroporous
5 ion exchange resin.

Aliphatic hydrocarbon residues containing 1 - 37 carbon atoms in formulae I and II com-
prise those which represent residues in compounds of interest in the flavour or fragrance
industry or which are intermediates in the manufacture of carotenoids and vitamins A in
10 their broadest sense. Under this aspect such residues encompass straight and branched
chain residues, saturated or ethylenically and/or ethinically unsaturated, which again
may be substituted with lower alkyl groups, particularly methyl or ethyl groups, or with C₃-
6-cyloalkyl and -cycloalkenyl groups, or which may contain such cyclic residues within the
carbon chain. In preferred embodiments residue R⁴ is a 2-(2'2'-dimethylcyclopropyl)-ethyl
15 group, a group represented by formula (A) = -[(CH₂)₃-CH(R⁵)]_x-CH₃ or formula (B) = -
[CH₂-CH₂-CH=C(R⁵)]_y-CH₃, wherein x and y are 1 - 6, preferably 1 - 4, and R⁵ is hydro-
gen, methyl or ethyl. Preferred examples of such groups are -(CH₂)₃-CH(CH₃)-(CH₂)₃-
CH(CH₃)₂ and -CH₂-CH₂-CH=C(CH₃)₂.

20 The expressions "basic anion exchange resin" and "strongly basic anion exchange resin"
are well known to persons skilled in the art of ion exchange, and many useful review ar-
ticles concern ion exchangers, inter alia strongly basic anion exchange resins such as in
Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 14 (1989), "Ion Exchangers",
pages 394 - 459, of which pages 397 - 400 are particularly pertinent regarding different
25 types of resins, cross-linking, porosity and exchange capacity. In general, ion exchange
resins featuring quaternary ammonium groups are strongly basic, and both "type I (or 1)"
and "type II (or 2)" resins are suitable for use in the process of the present invention, pro-
vided they are also "macroporous". The latter term as used herein denotes any resin
which has a higher degree of cross-linking than a gel resin (such as AMBERLITE® IRA
30 400). The pore diameter in a typical macroporous resin is about 100 nm as compared to
about 1 nm in a gel resin (see, besides Ullmann's Encyclopedia, supra, DIN 54 400,
"Ionenaustausch-Begriffe", 1987, p. 7). Apart from the many sources of information in
the scientific literature, the catalogues of suppliers of ion exchangers categorize their

products appropriately such that selecting a "strongly basic, macroporous anion exchange resin" for use in the process of the present invention is no problem for a person skilled in the art.

- 5 For the purpose of the present invention, the preferred strongly basic macroporous anion exchange resins are those featuring a polystyrene matrix with quaternary ammonium cations and hydroxyl anions supplied by several producers, e.g., by Röhm & Haas Deutschland GmbH, Frankfurt/Main, Germany; Purolite Company, Bala Cynwyd, Pennsylvania, USA (representative: Staerke & Nagler AG, Zürich, Switzerland); Dow Chemical Co., Midland, Michigan, USA and Bayer AG, Leverkusen, Germany. Suitable strongly
10 basic macroporous anion exchange resins are known under the trademarks DUOLITE[®], AMBERLITE[®], PUROLITE[®], DOWEX[®], LEWATIT[®], etc. Strongly basic macroporous anion exchange resins featuring a polyacrylic matrix rather than a polystyrene matrix can also be used in the process of the present invention but are less preferred than those
15 with a polystyrene matrix.

- Especially preferred in the isomerization of the present invention are basic anion exchange resins Amberlite[®] IRA 900, Dowex[®] MSA-1, Diaion[®] HPA25 or PA308 as well as Amberlysts[®] A260H, XE-4, XE-8, XE-8 new and XE-10 from Röhm & Haas and
20 equivalent resins with same chemical structure and similar physico-chemical properties.

- The amounts of resins to be used as catalysts can vary within wide ranges and depend on their physico-chemical structure. Optimal amounts can easily be determined empirically.

25

- The isomerization is conveniently carried out in a C₁₋₆-alcohol, preferably a C₁₋₃-alcohol, with methanol being preferred, at a temperature in the range of -10 °C to 30 °C, preferably in the range of 0 °C to 10 °C. The reactor is conveniently a fixed bed reactor. Since the isomerization is exothermic the reaction is effected under cooling according to
30 methods well-known in the art. In order to reduce undesirable heating (hot spots at the catalyst) it may be advantageous to dilute the catalyst by adding/mixing it with a neutral polymerisate, e.g., a macroporous polystyrene cross-linked with divinylbenzene without functional groups, such as MN270, obtainable from Purolite Company.

35 **Experimental part**

General:

All reactions were carried out under argon.

Flash chromatography (excess argon pressure ≤ 0.2 bar) was performed on Merck silica gel 60 (0.040-0.063 mm) and thin layer chromatography was performed on silica gel F254 plates; detection by UV (254 nm) and by spraying with a vanillin revelator (prepared from the sequential addition of 22 g vanillin, 830 g ethanol, 100 g ice and 100 mL of concentrated sulfuric acid) followed by heating with a heat gun.

Resins:

10

The wet A26OH, with R-NMe₃OH groups, was purchased from Rohm and Haas (Lot.0003260540); concentration of active sites >1.19 mmol/g; moisture holding capacity: 66 - 75 %. A26OH has a strong base capacity of 1.002 (mol/L), a total base capacity of 1.019 (mol/L), a total weight capacity of 4.007 (mmol/g) for the dry ion exchange resin and a moisture holding capacity of 68.01 %. XE-8-new has a strong base capacity of 0.681 (mol/L), a total base capacity of 0.783 (mol/L), a total weight capacity of 3.974 (mmol/g) for the dry ion exchange resin and a moisture holding capacity of 70.31 %. The catalysts were used as received. MN270, which is a macroporous polystyrene crosslinked with divinylbenzene, was purchased from Purolite and used as received.

20

Analyses:

NMR spectroscopy: at 298 K on Bruker Avance-300 spectrometer with CDCl₃ as solvent (Amar chemicals, stabilized with silver and containing 0.03 V/V% tetramethylsilane) at 300 MHz for ¹H-NMR and 75 MHz for ¹³C-NMR; chemical shifts δ in ppm relative to tetramethylsilane, coupling constants J in Hz. Quantitative ¹H-NMR were measured on Bruker Avance-300 spectrometer with 1,4-dimethoxybenzene (DMB; Fluka) as internal standard for the analyses of (1), (2) and (3).

30

Quantitative GC analysis of (4) was carried out with a gas chromatograph HP 6890 [capillary column Agilent DB-1701 (fused silica); 30 m x 0.32 μ m, film 0.1 μ m, 1.5 mL/min He, T = 70 °C for 1 min, 10 °C/min, 280 °C for 7 min] equipped with an autosampler HP 7683, split injector and FID; tR in min.

35

GC analysis of (6) was performed with a gas chromatograph HP 6890 [capillary column Optima-1 (fused silica), 30 m x 0.53 μ m, film 3.0 μ m, 3.6 mL/min He, T = 50 °C for 10

min, 6.0 °C/min for 11.67 min, 10 °C/min for 18 min] equipped with an autosampler HP 7683, split injector and FID; tR in min.

GC-MS analysis was performed with a HP 6890 [capillary column Restek Rtx5 SilMS with 5 % phenyl methyl silicone (fused silica), 30 m x 0.28 mm, film 0.5 µm, 1.50 mL/min He, T = 70 °C, 10.0 °C/min for 15 min] and EI at 70 eV.

Apparatus (Fig. 1):

Pumps of Gilson type 305, a Huber thermostat type "ministat", and a double-walled fixed-bed glass reactor (with a frit (porosity 0), length 18.5 cm, 6 mm inner diameter) were used.

The following Examples illustrate the present invention in more detail.

15

Example 1

(a) Isomerization of 6,10,14-trimethyl-pentadeca-4,5-dien-2-one (1) in batch mode to 6,10,14-trimethyl-pentadeca-3,5-dien-2-one (2).

20

In a 25 mL two-neck-flask equipped with a septum and an argon bubbler, the basic ion exchange resin A26OH (0.25 g, ≥ 0.3 mmol) was stirred in methanol (ca. 3 mL) for 15 minutes. The solvent was removed by pumping it out with a micro-filtercandle. Methanol (2.5 mL) was added to the catalyst and cooled down to an inner temperature of 1 - 3 °C (ice bath). The β -keto allene (1) (5.00 g with a purity 70.4 wt%, 13.31 mmol) was then added drop-wise within 5 minutes by syringe to the stirred catalyst. The temperature reached 6 °C. After the addition the reaction mixture was stirred below 25 °C. After 120 min of reaction the solution was separated from the catalyst by pumping it out with a micro-filter candle. The catalyst was washed two times with 3 mL methanol and could then be used for the next run. The methanol solution containing the crude product was concentrated in vacuo (40 mbar, 40 °C). The isolated yellow oil was analyzed by quantitative ¹H-NMR (formed (3E)-(2), (3Z)-(2) and remaining (1) with DMB as internal standard. The results are indicated in Table 1.

25
30

run	(3E) / (3Z)-(2) ratio	total yield [%]	remaining (1) [%]	conversion [%]	selectivity [%]
1	85 / 15	87.99	0.55	99.45	88.48
2	100 / 0	89.30	0.99	99.01	90.19
3	101 / -1	89.52	1.79	98.21	91.15
4	100 / 0	91.73	1.87	98.13	93.48
5	99 / 1	90.54	1.32	98.68	91.75
6	99 / 1	90.37	2.25	97.75	92.45
7	100 / 0	88.53	2.81	97.19	91.09
8	99 / 1	91.72	2.84	97.16	94.40
9	99 / 1	92.58	4.73	95.27	97.18
10	99 / 1	89.17	6.14	93.86	95.00

Table 1.

5 (b) Isomerization of (1) to (2) in continuous reaction mode.

A vertical double-walled fixed-bed glass reactor (with a frit, porosity 0, length 18.5 cm, 6 mm inner diameter) was cooled at 20 °C with a thermostat. The upper part of the reactor was connected through a T-junction to two Gilson pumps by Teflon tubes. The lower part of the reactor was connected to a bottle with a Teflon tube. The catalyst A26OH (0.50 g, ≥ 0.60 mmol) and MN270 (1.00 g; a macroporous polystyrene crosslinked with divinylbenzene, used to dilute the catalyst) were stirred in ca. 10 mL of methanol for 15 minutes and then transferred into the reactor. The level of the solution in the reactor was kept over the catalyst bed ($h = 4.5$ cm, $V = 5.1$ mL), controlled by siphon effect. The β -keto al-

15 lene (1) (purity 85.3 %) and methanol were separately pumped with a flow rate of 0.09 and 0.04 mL/min, respectively, into the two horizontal inlets of the T-junction fixed on the top of the continuous reactor. The so formed solution of 14 (17.10 mmol/mL) in methanol flew from the T-junction outlet into the reactor. Samples were taken regularly, concentrated in vacuo (40 mbar, 40 °C) and analyzed by quantitative ^1H -NMR. The feeding was

20 stopped after 24 hours. The solvent of the collected solution was evaporated in vacuo (40 mbar, 40 °C) and the isolated yellow oil analyzed by quantitative ^1H -NMR (formed (3E)-(2), (3Z)-(2) and remaining (1) with 1,4-dimethoxybenzene (DMB) as internal standard). The results are indicated in Table 2.

time [min]	(3 <i>E</i>) / (3 <i>Z</i>)-(2) ratio	total yield [%]	remaining (1) [%]	conver- sion [%]	selectivity [%]
195	99 / 1	94.50	5.42	94.58	99.90
435	100 / 0	90.78	7.70	92.30	98.35
615	99 / 1	90.09	8.54	91.46	98.51
795	99 / 1	88.00	11.91	88.09	99.90
1035	98 / 2	86.02	13.88	86.12	99.89
1215	97 / 3	82.22	17.70	82.30	99.90
1440	97 / 3	78.07	21.33	78.67	99.24
total	99 / 1	89.50	10.97	89.03	99.41

Table 2.

- 5 The apparatus is shown in Fig 1.

Example 2

- 10 Isomerization of 6,10-dimethyl-undeca-4,5,9-trien-2-one (3) to 6,10-dimethyl-undeca-3,5,9-trien-2-one (4) in repeated batch mode.

- In a 25 mL two-neck-flask equipped with a septum and an argon bubbler, the basic ion exchange resin A26OH (0.25 g, ≥ 0.3 mmol) was stirred in methanol (ca. 3 mL) for 15 minutes. The solvent was removed by pumping it out with a micro-filtercandle. Methanol (2.5 mL) was added to the catalyst and cooled down to an inner temperature of 1 - 3 °C (ice bath). The β -keto allene (3) (7.08 g with a purity of 91 %, 33.2 mmol) was added drop-wise within 10 minutes by syringe to the stirred catalyst. The temperature reached 6 °C. After the addition the reaction mixture was stirred between 1-3 °C. After 180 minutes of reaction the solution was separated from the catalyst by pumping it out with a micro-
 20 filter candle. The catalyst was washed two times with 3 mL of methanol and could then be used for the next run. The mixture containing the crude product was concentrated in vacuo (40 mbar, 40 °C). The isolated yellow oil was analyzed by quantitative GC (for (5*Z*)-(4) : (5*E*)-(4) ratio and yield determination). The results are indicated in Table 3.

run	(5Z) / (5E)-4 ratio	total yield [%]	remaining (3) [%]	conversion [%]	selectivity [%]
1	61 / 39	94.27	0.00	100.00	94.27
2	61 / 39	95.72	0.00	100.00	95.72
3	61 / 39	94.75	0.93	99.07	95.64
4	61 / 39	92.24	1.42	98.58	93.57
5	61 / 39	92.19	3.00	97.00	95.04
6	61 / 39	87.08	6.57	93.43	93.20
reactivation					
7	62 / 38	81.48	0.00	100.00	81.48
8	61 / 39	83.90	3.81	96.19	87.22
9	61 / 39	77.24	10.07	89.93	85.88

Table 3.

- 5 Reactivation of the catalyst was carried out when the yield was lower than 50 %. The catalyst was reactivated by addition of 2 mL of aqueous 1 M sodium hydroxide, stirring for 30 minutes, removal of the solution by pumping it into a gas washing flask with a micro-filter candle. The ion exchange resin was then stirred in 2 mL of distilled water for 5 minutes and the solution was removed. This was repeated four more times. The pH was
- 10 neutral for the third and fourth repeat. The catalyst was finally stirred in 2 mL of methanol for 15 minutes.

With basic exchange resin XE-8-new, the same procedure was used for the repeated batch isomerization with 7.08 g of (3) (purity 86 %, 31.3 mmol). Results are given in Table 4.

15

run	(5Z) / (5E)-4 ratio	total yield [%]	remaining (3) [%]	conversion [%]	selectivity [%]
1	62 / 38	96.67	0.00	100.00	96.67
2	62 / 38	96.92	4.00	98.57	98.33
3	62 / 38	93.44	6.00	94.00	99.40

Table 4

First reactivation: addition of 2 mL of aqueous 1 M sodium hydroxide, stirring for 35 minutes, removal of the solution by pumping it into a gas washing flask with a micro-filter candle. The ion exchange resin was then stirred in 2 mL of distilled water for 5 minutes and the solution was removed. This was repeated four more repeat. The pH was neutral
 5 for the fourth and fifth times. The catalyst was finally stirred in 2 mL of methanol for 15 minutes at least. Second reactivation: addition of 2 mL of aqueous 1 M sodium hydroxide, stirring for 17 hours, removal of the solution by pumping it into a gas washing flask with a micro-filter candle. The ion exchange resin was then stirred in 2 mL of distilled water for 1 hour and the solution was removed; this was repeated two more times. The pH
 10 was neutral for the second repeat. The catalyst was finally stirred two times in 2 mL of methanol for 1 hour. Then methanol was added for the next run.

Example 3

15 Isomerization of 6-methyl-hepta-4,5-dien-2-one (5) to 6-methyl-hepta-3,5-dien-2-one (6) in batch mode.

In a 25 mL two-neck-flask equipped with a septum and an argon bubbler, the basic ion exchange resin A26OH (0.25 g, ≥ 0.3 mmol) was stirred in methanol (ca. 3 mL) for 15
 20 minutes. The solvent was removed by pumping it out with a micro-filter candle. Methanol (2.5 mL) was added to the catalyst and cooled down to an inner temperature of 1 - 3 °C (ice bath). The β -keto allene (5) (4.62 g with a 90 % area GC, 33.5 mmol) was then added drop-wise by syringe to the stirred catalyst. The inner temperature was maintained between 1 - 9 °C. After 75 minutes no 5 could be detected by GC. The solution
 25 was separated from the catalyst by pumping it out with a micro-filter candle. The catalyst was washed two times with 3 mL of methanol. The mixture containing the crude product was concentrated in vacuo (40 mbar, 40 °C) affording a yellow oil (4.72 g). Purification of 1.54 g by flash chromatography (hexane/ethyl acetate 97:3, $R_f = 0.11$) allowed to recover 1.16 g (75 %) of purified (6). Coconut smell.

30

GC: (Z)-6 $t_R = 25.00$ and (E)-6 $t_R = 26.26$. (E/Z) 95:5

$^1\text{H-NMR}$ of (E)-6: 1.90 (s, 3H, $\text{CH}_3\text{-C-CH}_3$), 1.92 (s, 3H, $\text{CH}_3\text{-C-CH}_3$), 2.27 (s, 3H, $\text{CH}_3\text{C=O}$), 6.00 (d, $J=12$ Hz, 1H, $(\text{CH}_3)_2\text{C=CH}$), 6.01 (d, $J=15$ Hz, 1H, O=C-CH=), 7.42 (dd, $J=12$ Hz, $J=15$ Hz, 1H, $=\text{CH-CH=CH}$).

35 $^{13}\text{C-NMR}$ (E)-6: 19.0 ($\text{CH}_3\text{-C}$), 26.6 ($\text{CH}_3\text{-C}$), 27.4 ($\text{CH}_3\text{-CO}$), 124.1 ($(\text{CH}_3)_2\text{C=CH}$), 128.0 (O=C-CH=), 139.5 ($=\text{CH-CH=CH}$), 147.5 ($\text{C-(CH}_3)_2$), 198.7 (CO).

An analytic sample was prepared according to the procedure of Saucy and Marbet (Helv. Chim. Acta 1967, 50, 1158 - 67 [1]).

GC: (Z)-(6) t_R = 25.00 and (E)-(6) t_R = 26.26. (E/Z) 87:13 (Lit.: 86:14 [1])

GC-MS: (Z)-(6) t_R = 5.44, m/z 43, 81, 109 [$M^+ - CH_3$], 124 [M^+].

5 (E)-(6) t_R = 6.22, m/z 43, 81, 109 [$M^+ - CH_3$], 124 [M^+].

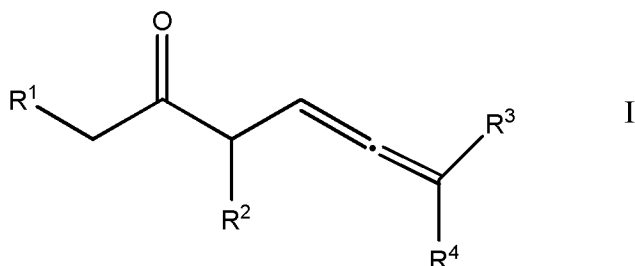
Example 4

10 Comparison of A260H resin in batch experiments with NaOH according to method of Saucy and Marbet [1967].

The comparison of A260H in batch experiments with NaOH shows two main trends:
The turnover numbers (TON) were higher with A260H for (3) to (4), viz. 620 (for 6 runs) versus 94 (used only once). The turnover frequencies (TOF) were lower with A260H for
15 (3) to (4), viz. 34 h^{-1} (for 6 runs) versus 188 h^{-1} . Independent from the catalyst used in the isomerization the reaction is faster with smaller alkyl chains in the keto allene.

Claims

1. Isomerization of β -keto-allenes of the general formula



5

wherein R^1 is hydrogen, methyl or ethyl, in particular hydrogen or methyl;

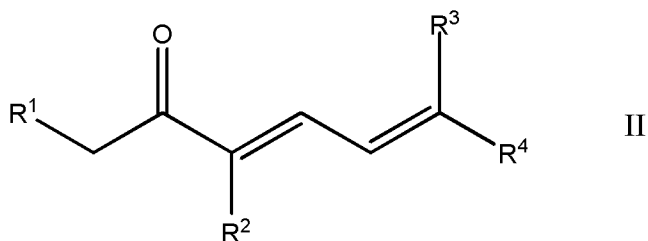
R^2 is hydrogen or methyl;

R^3 is hydrogen or methyl, in particular methyl and

R^4 is an aliphatic hydrocarbon residue containing 1 – 37 carbon atoms,

10

into corresponding α,γ -dienones of formula



15 by treatment with a basic ion exchange resin.

2. The isomerization of claim 1 wherein the basic ion exchange resin is a strongly basic, macroporous resin.

20 3. The isomerization of claim 1 or claim 2, wherein in formula I R^4 is 2-(2'2'-dimethylcyclopropyl)-ethyl.

4. The isomerization of claim 1 or claim 2, wherein in formula I R^4 is a residue A = $-(CH_2)_3-CH(R^5)-CH_3$ with R^5 = hydrogen, methyl or ethyl and x = whole number from 1
25 to 6.

5. The isomerization of claim 1 or claim 2, wherein in formula I R⁴ is a residue B = $-\text{[CH}_2\text{-CH}_2\text{-CH=C(R}^5\text{)]}_y\text{-CH}_3$ with R⁵ = hydrogen, methyl or ethyl and y = whole number from 1 to 6.
- 5 6. The isomerization of claim 1 or claim 2, wherein the compound of formula I is 6,10,14-trimethyl-pentadeca-4,5-dien-2-one.
7. The isomerization of claim 1 or claim 2, wherein the compound of formula I is 6,10-dimethyl-undeca-4,5,9-trien-2-one.
- 10 8. The isomerization of claim 1 or claim 2, wherein the compound of formula I is 6-methyl-hepta-4,5-dien-2-one.
9. The isomerization of any one of claims 1 to 8 wherein the basic anion exchange
15 resin is of type 1 or of type 2.
10. The isomerization of any one of claims 1 to 9 which is run in continuous mode with regeneration of the anion exchange catalyst.

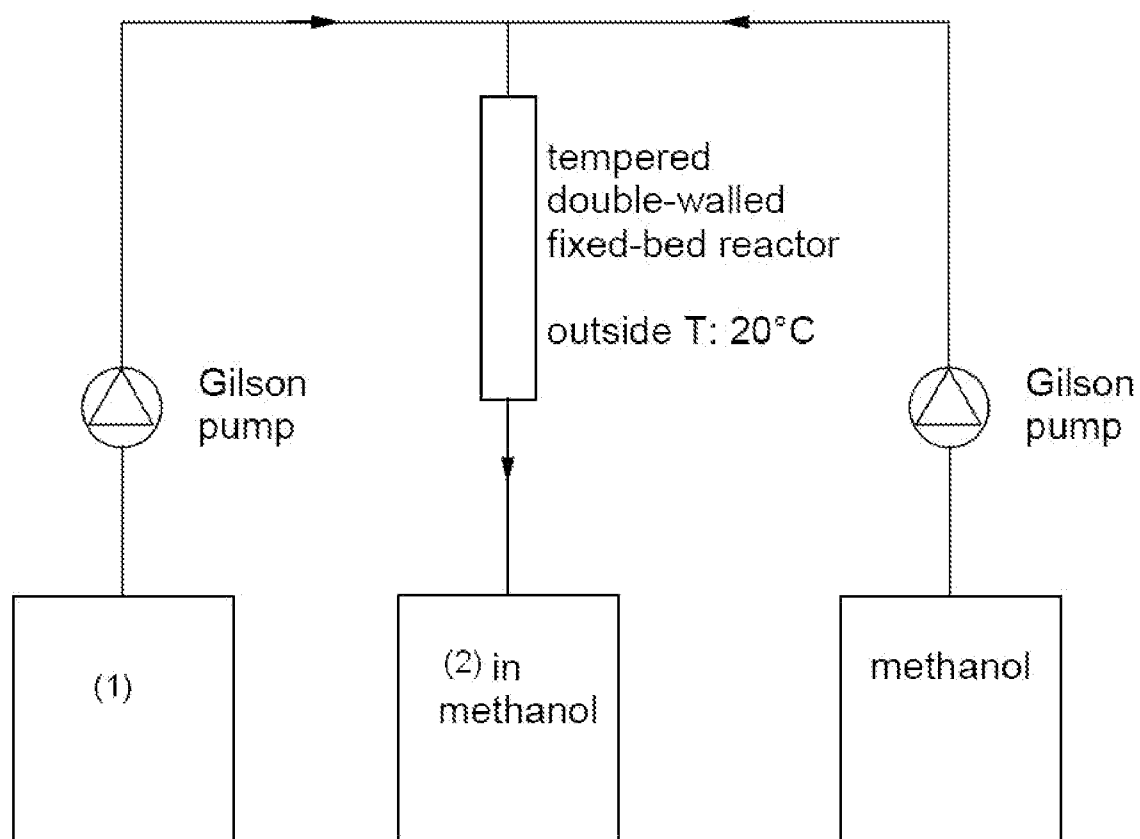


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/056106

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C49/203

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JULIA S ET AL: "Mémoires présentés a la société chimique.Nr.-517.-Transposition homoallylique vinylogue d alcools Alpha,Bêta,Gamma,Delta-diéniques Epsilon-cyclopropaniques", BULLETIN DE LA SOCIETE CHIMIQUE DE FRANCE, SOCIETE FRANCAISE DE CHIMIE. PARIS, FRANCE, 1 January 1964 (1964-01-01), pages 3218-3226, XP009087142, ISSN: 0037-8968 page 3221, preparation of 4a -----	1-10
A	EP 0 647 624 A1 (RHONE POULENC NUTRITION ANIMAL [FR]) 12 April 1995 (1995-04-12) example 9 ----- -/--	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

27 September 2011

Date of mailing of the international search report

05/10/2011

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/056106

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/092655 A1 (DSM IP ASSETS BV [NL]; BONRATH WERNER [DE]) 7 August 2008 (2008-08-07) example 6 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/056106

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		DE 69404932 T2 22-01-1998	
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