

1

3,655,768

## PRODUCTION OF ALK-1-EN-6-ONES

Horst Pommer, Ludwigshafen, Herbert Mueller, Frankenthal, and Hermann Overwien, Ludwigshafen, Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany  
No Drawing, Filed Nov. 13, 1968, Ser. No. 775,518  
Int. Cl. C07c 49/20, 49/45, 49/76  
U.S. Cl. 260—593 R

9 Claims

### ABSTRACT OF THE DISCLOSURE

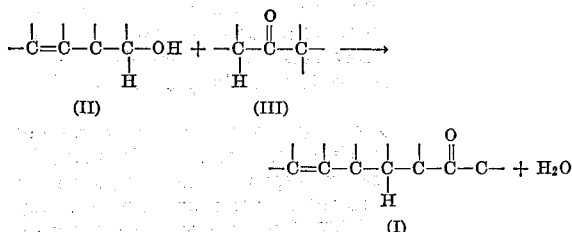
Production of alk-1-en-6-ones by reaction of an alk-1-en-4-ol at from 100° to 400° C. with a ketone bearing at least one hydrogen atom on a carbon atom in vicinal position to the carbonyl group.

The present invention relates to a new process for the production of alk-1-en-6-ones (I).

Since these compounds have usually been accessible with difficulty and by uneconomical methods, attempts have been made to find a simple and widely applicable method for their production.

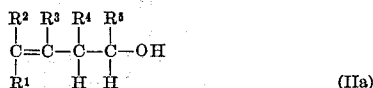
We have found that the said compounds (I) are obtained when an alk-1-en-4-ol (II) is reacted at from 100° to 400° C. with a ketone (III) which bears at least one hydrogen atom on a carbon atom adjacent to the carbonyl group.

The process can be represented by the following equation:

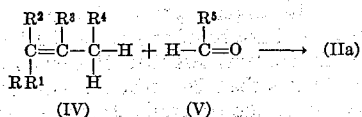


The free valencies in the formulae are occupied by hydrogen or hydrocarbon radicals.

Among the alk-1-en-4-ols (II) to be used as starting materials, those are particularly suitable which have the general formula (IIa)



where the radicals R<sup>1</sup> to R<sup>5</sup> denote hydrogen or aliphatic, cycloaliphatic, araliphatic or aromatic hydrocarbon groups having up to eight carbon atoms, some of these groups if desired being linked together in pairs to form five-membered to seven-membered rings. Especially suitable compounds are those in which four of the radicals R<sup>1</sup> to R<sup>5</sup> denote hydrogen atoms and the remaining radical is one of the said hydrocarbon groups. A large number of compounds (IIa) is easily accessible by reaction of olefins (IV) with aldehydes (V) as shown:



Preferred starting materials (IIa) are those having four to ten carbon atoms, for example but-1-en-4-ol, 2-methylbut-1-en-4-ol, 3-methylbut-1-en-4-ol, pent-2-en-5-ol and 2-cyclohexylbut-1-en-4-ol. The compounds but-1-en-4-ol and

2

2-methylbut-1-en-4-ol have particular industrial importance.

Particularly suitable ketones (III) are those having the general Formula IIIa:



where the radicals R<sup>6</sup> to R<sup>10</sup> each denotes a hydrogen atom or an aliphatic, cycloaliphatic, araliphatic or aromatic hydrocarbon group having up to eight carbon atoms, these groups if desired being combined in pairs to form five-membered to seven-membered rings. Preferred compounds (IIIa) are those having from three to eight carbon atoms, for example acetone, methyl ethyl ketone, diethyl ketone, cyclohexenyl methyl ketone and acetophenone. Diethyl ketone and acetone have particular industrial importance.

When the ketone (III) is unsymmetrical and bears at least one hydrogen atom on both of the carbon atoms adjacent to the carbonyl group, a mixture of two different compounds (I) is obtained.

According to observations made so far, the success of the process according to this invention is not perceptibly dependent on the nature of the substituents on (II) and (III), particularly on (IIa) and (IIIa) provided it is borne in mind that the reaction rate generally decreases as the molecular size of these compounds increases. Undesired secondary reactions, in particular the polymerization of (I) and (II) or (IIa) or the intramolecular elimination of water from (II) or (IIa), may be suppressed as usual by operating in the presence of polymerization inhibitors or in the presence of water under pressure. Moreover, it is often advisable to accelerate the reaction in the desired direction by using one of the reactants in an excess of up to twenty times.

The preferred reaction temperatures are from 200° to 350° C. Since most of the starting materials (II) and (III) which have special importance industrially would be gaseous at these temperatures at atmospheric pressure and since the reaction in liquid phase is preferred, it is preferable to use superatmospheric pressure (up to about 1000 atmospheres), preferably the vapor pressure which is set up above the reaction mixture at the temperature chosen.

Since the products (I) of the process are themselves ketones which fall under the definition for (III) and thus can undergo further reaction, it is advantageous to aim at low conversions or to use a large excess of (III). This procedure may best be carried out semicontinuously or continuously by a conventional method.

The reaction may be carried out with or without inert solvents or diluents but in general one of the reactants serves as solvent.

When water is used as solvent or diluent, it is advantageous to maintain a constant pH value of from about 5 to 8 by means of buffer substances.

Many alk-1-en-6-ones are accessible by the process according to this invention and some of them are valuable perfumes or can be used as intermediates for the synthesis of the same.

The invention is illustrated by the following examples.

### EXAMPLE 1

290 g. (5 moles) of acetone and 70 g. (0.8 mole) of 2-methylbut-1-en-4-ol are heated in an autoclave for forty-five minutes, a pressure of about 220 atmospheres being set up. The reaction mixture is worked up by distillation. 42 g. of 2-methylhept-1-en-6-one passes over and 30 g. of 2-methylbut-1-en-4-ol is recovered. This is a yield of 72% with reference to the conversion; the conversion itself is 57%.

3

## EXAMPLE 2

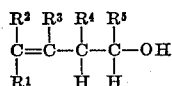
290 g. (5 moles) of acetone and 73 g. (1 mole) of but-1-en-4-ol are heated for one hour at 270° C. in an autoclave, a pressure of about 250 atmospheres being set up. The reaction mixture is worked up by distillation; hept-1-en-6-one is obtained in a yield of 63% with reference to a conversion of 50%.

## EXAMPLE 3

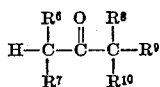
280 g. (3.2 moles) of diethyl ketone and 70 g. (0.8 mole) of 2-methylbut-1-en-4-ol are heated for forty-five minutes at 300° C., a pressure of about 250 atmospheres being set up. The reaction mixture is worked up by distillation; 2,5-dimethyloct-1-en-6-one is obtained in a yield of 48% with reference to a conversion of 39%.

We claim:

1. A process for the production of an alk-1-en-6-one which comprises reacting, at from 100° to 400° C., an alk-1-en-4-ol of the formula:



wherein each of the radicals R<sup>1</sup> to R<sup>5</sup> when taken alone denotes a hydrogen atom or an aliphatic, cycloaliphatic or aromatic hydrocarbon radical having up to eight carbon atoms and wherein two of the radicals R<sup>1</sup> to R<sup>5</sup> when taken together form a five- to seven-membered carbocyclic ring and wherein the alk-1-en-4-ol contains a total of from four to ten carbon atoms, with a ketone of the formula:



wherein each of the radicals R<sup>6</sup> to R<sup>10</sup> when taken alone denotes a hydrogen atom or an aliphatic or cycloaliphatic

4

hydrocarbon radical and wherein two of the radicals R<sup>6</sup> to R<sup>10</sup> when taken together form a five- to seven-membered carbocyclic ring and wherein the ketone contains a total of from three to eight carbon atoms.

2. A process as claimed in claim 1 wherein four of the radicals R<sup>1</sup> to R<sup>5</sup> denote hydrogen atoms and the remaining radical denotes one of the said hydrocarbon radicals.

3. A process as claimed in claim 1 wherein but-1-en-4-ol or 2-methylbut-1-en-4-ol is used as the alk-1-en-4-ol.

4. A process as claimed in claim 1 carried out at from 200° to 350° C.

5. A process as claimed in claim 1 carried out at a pressure of up to about 1000 atmospheres.

6. A process as claimed in claim 1 wherein said ketone reactant is selected from the group consisting of diethyl ketone and acetone.

7. A process as claimed in claim 1 wherein the ketone reactant is acetone and the alkenol reactant is 2-methylbut-1-en-4-ol.

8. A process as claimed in claim 1 wherein the ketone reactant is acetone and the alkenol reactant is but-1-en-4-ol.

9. A process as claimed in claim 1 wherein the ketone reactant is diethyl ketone and the alkenol reactant is 2-methylbut-1-en-4-ol.

## References Cited

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DANIEL D. HORWITZ, Primary Examiner

U.S. Cl. X.R.

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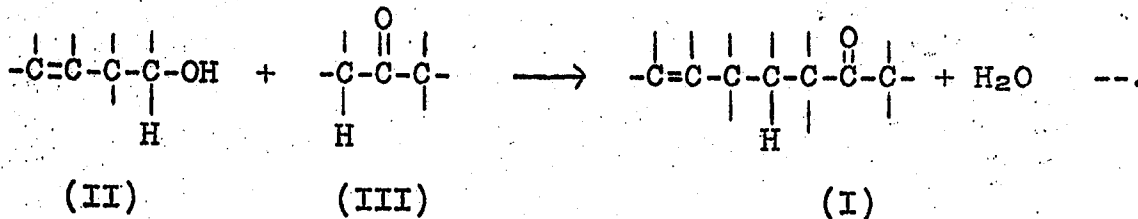
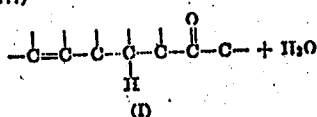
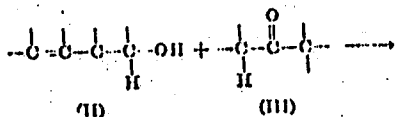
UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,655,768 Dated April 11, 1972

Inventor(s) Horst Pommer, Herbert Mueller, and Hermann Overweil

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 8, in the heading, after "775,518" insert  
-- Claims priority, application Germany, November 17, 1967,  
P 16 43 696.7 --; lines 33 to 42,  
" " should read



Signed and sealed this 28th day of November 1972.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents