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USE OF OXO-METALLIC DERIVATIVES IN ISOMERISATION

REACTIONS OF UNSATURATED ALCOHOLS

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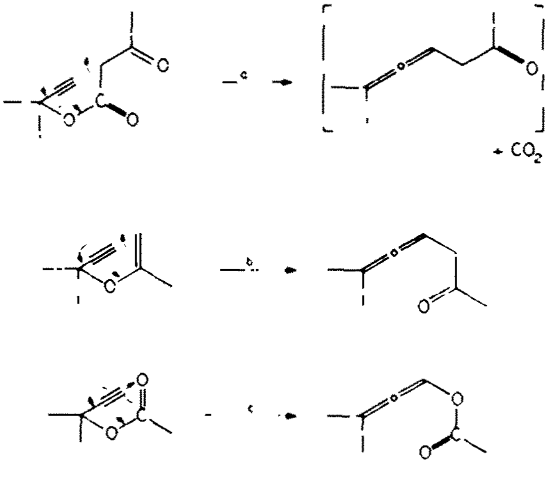
Abstract—The isomerisation of α-acetylenic alcohols to ethylenic carbonyl derivatives and the isomerisation of α-ethylenic alcohols to the corresponding allyl alcohols may be effected in good yields in a single step using oxometallic derivatives. The vanadate esters are particularly efficient. Mechanistic explanations are given.

The problems of the isomerisation of α-acetylenic alcohols to ethylenic carbonyl derivatives and of the rearrangement of α-ethylenic alcohols to corresponding allyl alcohols by a more economical and simpler catalytic method than those hitherto known presented themselves to us in 1967. The isomerisation of acetylenic alcohols in a single stage had only found solutions in isolated cases.[1] Isomerisations in several stages, using various intermediates derived from the alcohols, had also been carried out, amongst which may be mentioned those leading to allene acetates, namely the reaction of 3-chloro-3-methyl-butyne with silver acetate in acetic acid, giving 2-acetoxy-3-methyl-buta-1,2-diene[2] and the isomerisation of acetates of acetylenic tertiary alcohols, by pyrolysis[3] or by heating in acetic acid in the presence of silver salts.[4] (For a review of these isomerisation reactions, see Ref. [5]).

The isomerisation of ethylenic alcohols by means of acid catalysts which bring about the allyl rearrangement was known.[6,7] This type of reaction, which sometimes lacks selectivity, was also capable of being carried out in several stages, such as acetylation, isomerisation and saponification. (For this reason, the conversion of nerolidol to farnesol was carried out with mediocre yields[7]). It was thus of interest to investigate isomerisation catalysts which do not exhibit the disadvantages described above.

Isomerisation of α-ethylenic and α-acetylenic alcohols by means of oxo-metallic derivatives

In the Carroll rearrangement of acetylenic esters (a), the Claisen rearrangement of enol ethers (b) and the rearrangement of esters of acetylenic tertiary alcohols (c), [3.3] sigmatropic reactions occur with scission of the C–O bond and formation of a C–C or C–O bond. The reaction (c) only takes place satisfactorily in the presence of silver catalysts.[4]† We considered it probable that an ester of an inorganic acid, the metal of which would at the same time play the role of a catalyst, could have an advantageous effect on the reaction. We have used certain oxo-metallic derivatives (Table 1) to check this hypothesis.



These first results have led to several patents,[8,9] and to the construction, in 1972,[10] of an industrial unit for the isomerisation of dehydrolinalol to citral. Since the appearance of our patents, several groups have investigated the isomerisation of acetylenic alcohols in the presence of derivatives of vanadium[11,12] or other metals,[12] and have similarly studied ethylenic alcohols.[13]

Vanadate esters as catalysts for the isomerisation of α-ethylenic and α-acetylenic alcohols

Although derivatives of other metals, as molybdenum or rhenium gave interesting results the purpose of this communication is to report isomerisations by vanadate esters.

Preparation of the vanadates $O = V(OR)_3$. Equations (1)–(5), in which RO and R'O can be either an alkoxy or a siloxy group, show some ways in which these vanadates may be prepared. Thus, alcohols and silanols are equivalent from the point of view of the trans-esterification, this is the key of the catalytic action of the vanadates in this isomerisation reaction, as we shall see later.

(1) $Ag_3VO_4 + 3\,RI \rightarrow OV(OR)_3 + 3\,AgI$
(2) $V_2O_5 + 6\,ROH \rightarrow 2\,OV(OR)_3 + 3\,H_2O$
(3) $OVCl_3 + 3ROH + 3NH_3 \rightarrow OV(OR)_3 + 3NH_4Cl$
(4) $OV(OR)_3 + 3R'OH \rightleftarrows OV(OR')_3 + 3ROH$
(5) $OV(OR)_3 + 3CH_3COOR' \rightleftarrows OV(OR')_3 + 3CH_3COOR.$

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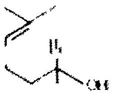
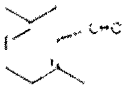
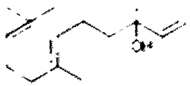
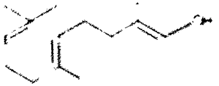
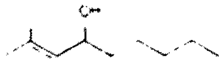
† Schmid *et al.*[14] have recently proposed the formation of a π-complex between the silver and either the triple bond of the propargyl ester starting material or the carbon–carbon double bond of the allene ester, thus allowing the [3.3] sigmatropic reaction to take place.

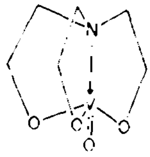
Table 1. Isomerisation of α-ethylenic and α-acetylenic alcohols by means of oxo-metallic derivatives

	Alcohol starting material	Isomers obtained	Catalysts	$\frac{\text{mols of catalyst}}{\text{mols of unsaturated alcohol}}$	Solvent	T°	Duration	Yield	Degree of conversion
1			NH_4VO_3 + cyclohexanol	6.6×10^{-3}	0	160°	30 min	65	30
2	"	"	"	6.6×10^{-3}	Paraffin oil*	160°	30 min	76	28
3	"	"	V_2O_5 alumina	1.1×10^{-2}	0	140°	2h	57	9
4	"	"	tris tetrabutyl ammonium decavanadate	6.8×10^{-4}	0	150°	2 h	67	26
5	"	"	Vanadyl acetylacetonate	6.8×10^{-3}	0	170°	35 min	41	43
6	"	"	Vanadyl acetate	1.4×10^{-2}	0	130°	2 h 15 min	50	37
7	"	"	Vanadyl hexahydrobenzoate	7.8×10^{-3}	0	130°	2 h 15 min	54	27
8	"	"	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ + cyclohexanol*	6.2×10^{-4}	Paraffin oil*	170°	15 min	46	18
9	"	"	$Mo(C_4H_8O_4)$ (MoO_3 + ethylene glycol)	9.4×10^{-3}	0	150°	2 h	38	39
10	"	"	NH_4ReO_4 + cyclohexanol	5.7×10^{-3}	0	170°	10 min	47	20
11			NH_4VO_3 + cyclohexanol	1.3×10^{-2}	0	150°	3 h	80	81
12	"	"	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ + cyclohexanol	2.5×10^{-3}	0	150°	1 h 30 min	63	85
13			$(NH_4)_{10}W_{12}O_{41}\cdot 7H_2O$ + cyclohexanol	8×10^{-4}	0	160°	7 h 30 min	22	12
14	"	"	$OW(OSi\Phi_3)_4$	3×10^{-3}	0	200°	3 h	74	30
15			$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ + cyclohexanol	3×10^{-3}	0	130°	2 h 50 min	80	28
16			NH_4VO_3	5.4×10^{-3}	0	130°	2 h 50 min	47	27

See table 3 for footnote.

Study of the isomerisation of dehydrolinalol to citral. Dehydrolinalyl orthovanadate was synthesised from ethyl orthovanadate and three equivalents of the dehydrolinalol, the equilibrium being shifted by removal of the ethanol formed (eqn 4). This orthovanadate decomposes on heating, giving a little citral and polyvanadates (by a mechanism given below). Its hydrolysis gives back dehydrolinalol. When heated in the presence of dehydrolinalyl orthovanadate, dehydrolinalol gives citral (60%) (Table 2), in accordance with the anticipated mechanism. It is thus possible to avoid the preparation of dehydrolinalyl orthovanadate for the isomerisation of dehydrolinalol by using vanadium derivatives such as alkyl vanadates, silanyl vanadates, polysiloxy vanadates and the like, which can produce the vanadate catalyst *in situ* by exchange.

Triethanolamine orthovanadate requires a special comment. This is one of the cyclic inorganic esters of the triethanolamines referred to as "atranes" by Voronkov *et al.*[3] Triethanolamine orthovanadate is an oxovanadatrane and possesses a nitrogen–vanadium coordination bond. It is a crystalline product sparingly soluble in dehydrolinalol at ambient temperature, and giving a homogeneous solution under the isomerisation conditions. At the end of the operation, the catalyst crystallises out on simple cooling and can be recovered by filtration.

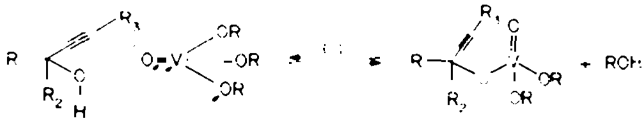


Isomerisation of various unsaturated alcohols. Tables 2 and 3 give some results which we obtained in isomerisations of α-acetylenic or α-ethylenic alcohols by means of vanadate esters.

Mechanism of the reaction

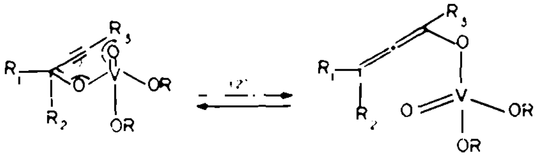
α-Acetylenic alcohols. From a vanadate $OV(OR)_3$, the discussion will be confined to a radical RO to facilitate writing (ROH represents an alcohol or an equivalent, for example a silanol, and R_1 can be H).

First stage: *trans*-esterification (1)



(I)

Second stage: [3,3] sigmatropic rearrangement (2)



Third stage: *trans*-esterification (3 or 3')

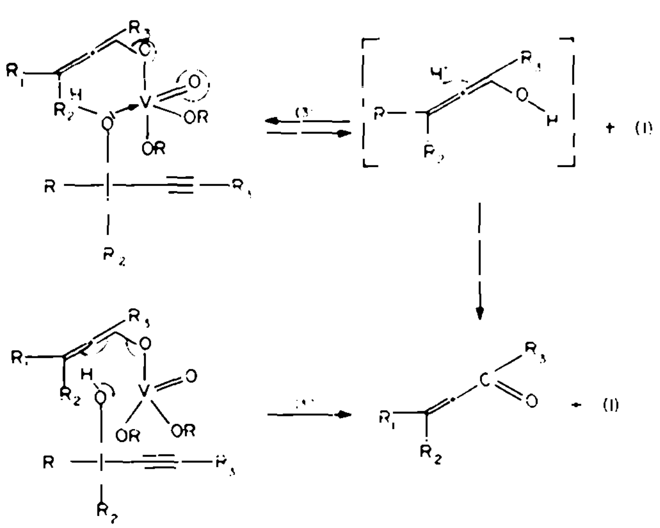
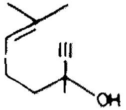
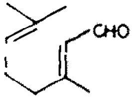
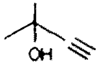
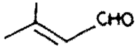
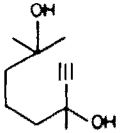
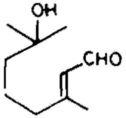
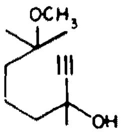
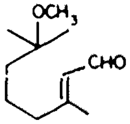
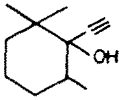
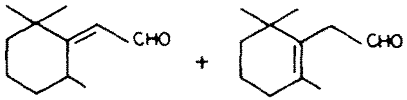
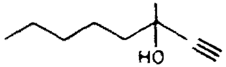
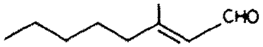
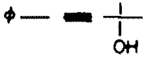
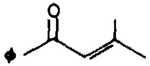
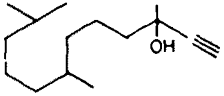
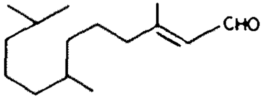


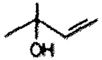
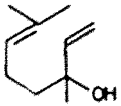
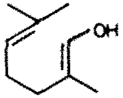
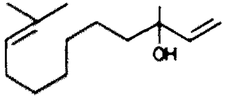
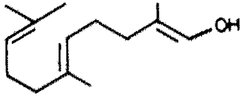
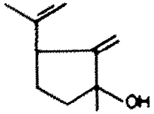
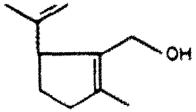
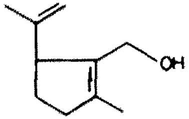
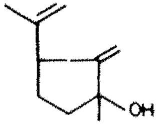
Table 2. Vanadate esters as catalysts for the isomerisation of α-acetylenic alcohols

	Alcohol starting material	Isomers obtained	Catalysts	$\frac{\text{mols of catalyst}}{\text{mols of unsaturated alcohol}}$	Solvent	T°	Duration	Yield	Degree of conversion
17			*n*-propyl orthovanadate	5×10^{-3}	0	130°	4 h	77^(a)	20
18	..	..	Isobutyl orthovanadate	2.2×10^{-2}	0	130°	30 min	67^(a)	22
19	..	..	Triethanolamine orthovanadate	3.9×10^{-3}	0	160°	35 min	75.7^(b)	21
20	..	..	Cyclohexyl orthovanadate	8×10^{-3}	0	125°	2 h	80^(b)	11
21	..	..	..	2.1×10^{-2}	Paraffin oil^(h)	125°	1 h	77^(b)	14
22	..	..	Tetrahydrolinalyl orthovanadate	3.9×10^{-3}	0	160°	30 min	77^(a)	21
23	..	..	..	7.7×10^{-3}	Paraffin oil^(h)	160°	30 min	69^(b)	23
24	..	..	Dehydrolinalyl orthovanadate	2.8×10^{-2}	0	140°	1 h	60^(b)	33
25	..	..	3,5-dimethyl/hexyl-3 orthovanadate	3.8×10^{-3}	0	160°	30 min	70^(b)	23
26	..	..	Trimethylsilyl orthovanadate	1.4×10^{-3}	0	160°	35 min	59^(a)	33
27	..	..	Triphenylsilyl orthovanadate	4.1×10^{-3}	0	160°	35 min	54^(a)	30
28			Tetrahydrolinalyl orthovanadate	8.4×10^{-3}	0	150°	2 h^(l)	88^(a)	23
29	..	..	Triphenylsilyl orthovanadate	6.2×10^{-2}	Paraffin oil^(i)	150°	2 h 30 min followed by 30 min^(m)	37^(a)	95
30			Triethanolamine orthovanadate	3.7×10^{-3}	0	160°	2 h	72^(b)	25

31				4.6×10^{3}	0	160°	2 hr 30 min	90[b]	39
32			Cyclohexyl orthovanadate	4.6×10^{2}	Paraffin oil[d]	130°	2 h 30 min	13 - 78[c]	61
33			Cyclohexyl orthovanadate + cyclohexanol[e]	3.8×10^{3}	0	120° to 160°	1 h 30 min	63[c]	44
34			Cyclohexyl orthovanadate	8.8×10^{3}	Paraffin oil[d]	145°	6 h	70[c]	100
35			Triethanolamine orthovanadate	3.8×10^{3}	0	160°	1 h 30 min	86[b]	37

See Table 3 for footnotes

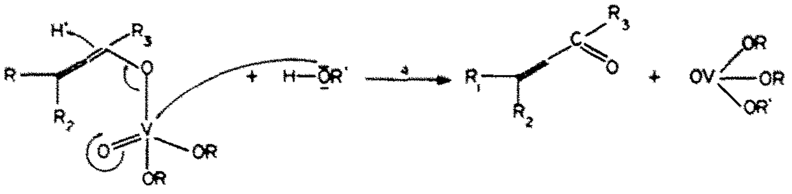
Table 3. Vanadate esters as catalysts for the isomerisation of α-ethylenic alcohols

	Alcohol starting material	Isomers obtained	Catalysts	mols of catalyst / mols of unsaturated alcohol	Solvent	T°	Duration	Yield	Degree of conversion
36			Tetrahydrolinalyl orthovanadate	1.7×10^{-3}	0	150°	7 h	83[a]	26
37			Tetrahydrolinalyl orthovanadate	7.7×10^{-3}	0	160°	1 h 30 min	85[a]	30
38	"	"	Triphenylsilyl orthovanadate	7.7×10^{-3}	0	160°	1 h 30 min	87[a]	31
39			Tetrahydrolinalyl orthovanadate	5.5×10^{-3}	0	160°	1 h	89[c]	22
40	"	"	Triethanolamine orthovanadate + tertiary butanol[n]	5.5×10^{-3}	0	170°	2 h	78[a]	30
41			Cyclohexyl orthovanadate	1.1×10^{-2}	0	78° to 132°	5 h	76[c]	19
42			Octadecyl orthovanadate	1×10^{-2}	0	160°	1 h 30 min	89[a]	68
43			Octadecyl orthovanadate	1×10^{-2}	0	160°	1 h 30 min	56[a]	34

(a) Chromatographic determination.
(b) Chemical determination.
(c) Estimation by nuclear magnetic resonance.
(d) mols of cyclohexanol/mols of unsaturated alcohol $= 7.7 \times 10^{-2}$.
(e) *mols of cyclohexanol/mols of unsaturated alcohol* $= 1.5 \times 10^{-1}$.
(f) mols of cyclohexanol/mols of unsaturated alcohol $= 4.4 \times 10^{-1}$.
(g) Weight relationships solvent/unsaturated alcohol = 1.
(h) Weight relationships solvent/unsaturated alcohol = 2.
(i) Weight relationships solvent/unsaturated alcohol = 7.3.
(j) Weight relationships solvent/unsaturated alcohol = 4.
(k) Calculated on V_2O_5.
(l) Operation carried out in an autoclave under autogenous pressure.
(m) Operation carried out in a flash, the alcohol to be isomerised being run in slowly (2.5 h).
(n) mols of tertiary butanol/mols of unsaturated alcohol $= 1.5 \times 10^{-1}$.

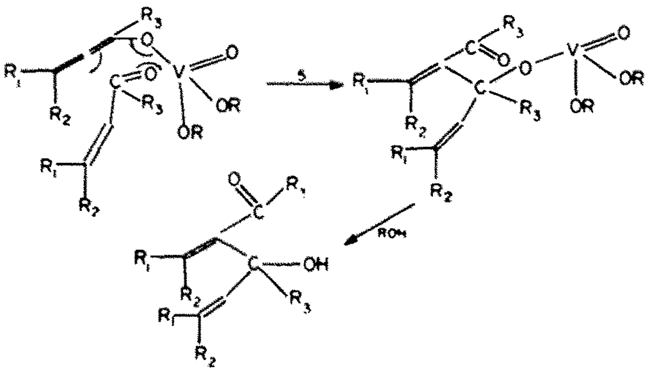
The vanadate (I) capable of producing the desired cyclic transfer is regenerated, and is therefore a catalyst; it can be recycled without losing activity or selectivity.

Influence of the presence of R'OH *in the mixture* (R'O = *alkoxy or siloxy*). In 3 or 3', R'OH competes, in the *trans*-esterification, with the acetylenic alcohol to be isomerised.



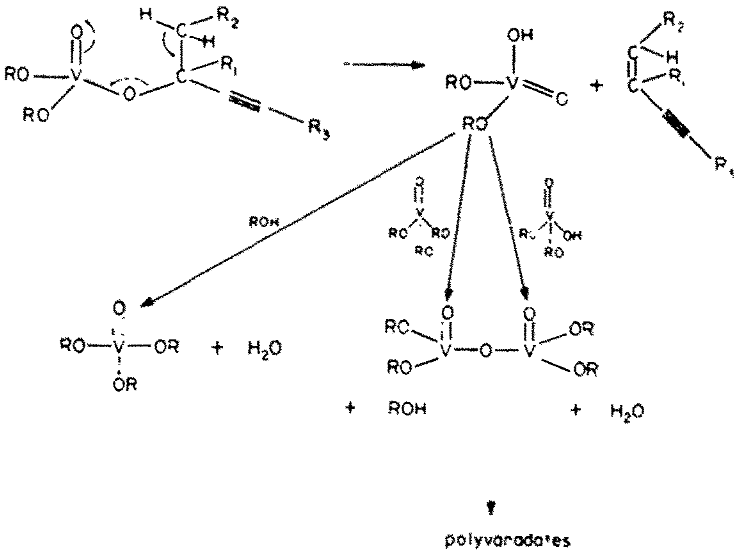
(R' may be identical to R).

This ensures the compound does not remain too long in form (II) which is responsible, as the concentration of carbonyl product increases, for the formation of non-volatile products, for example by the following mechanism.

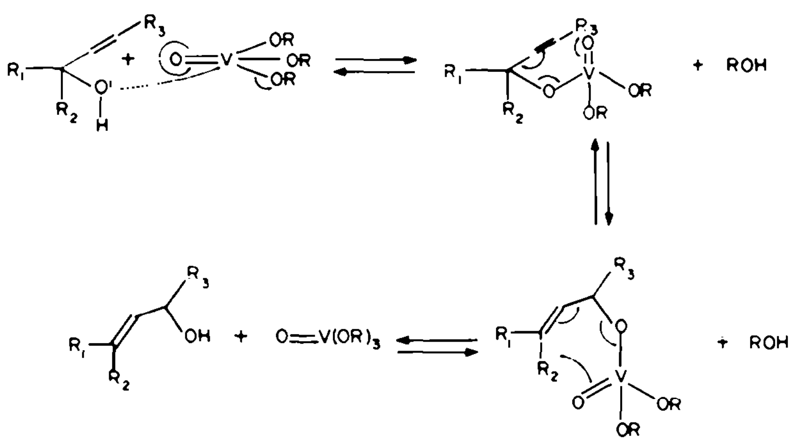


This type of side reaction can also be minimised in other ways. One can for instance use incomplete conversion; in this way, as the carbonyl product formed is present in a lower concentration than its acetylenic isomer, reactions 3 or 3' predominate over 5. Everything occurs as if the alcohol to be isomerised served as the solvent. One can also use a solvent which is inert towards the reactants.

It is possible to avoid another side reaction: the condensation of the vanadates with one another, leading to polyvanadates and to dehydration products of the alcohols (for example dehydromyrcen from dehydrolinalol) in accordance with an initial mechanism such as.



α-Ethylenic alcohols. If the triple bond is replaced by a double bond in the rearrangement mechanisms given above, the following equilibria result in a similar manner.



The explanation of certain side reactions in the case of the isomerisation of dehydrolinalol to citral is to be found within this framework.

It is known that dehydrolinalol can isomerise thermally by a [3,2] sigmatropic reaction, to give 1-hydroxy-1-methyl-2-methylene-3-isopropenyl-cyclopentane (see, e.g. Ref. [16]). We have shown that the product contains two isomers, the isopropenyl and hydroxyl groups being in the *cis*-position or *trans*-position relative to the cyclopentane. These epimers cannot be mutually equilibrated directly. On the other hand, the treatment of one or the other of these products with an oxo-metallic derivative, such as a vanadate, gives an intermediate ester which can, after [3,3] sigmatropic rearrangement and liberation of the alcohol group, lead to its primary allyl isomer. Conversely, the primary alcohol will give an ester, the rearrangement of which can give the mixture of the *cis* and *trans* tertiary alcohols. Ultimately, three isomers can thus be present and mutually equilibrated.

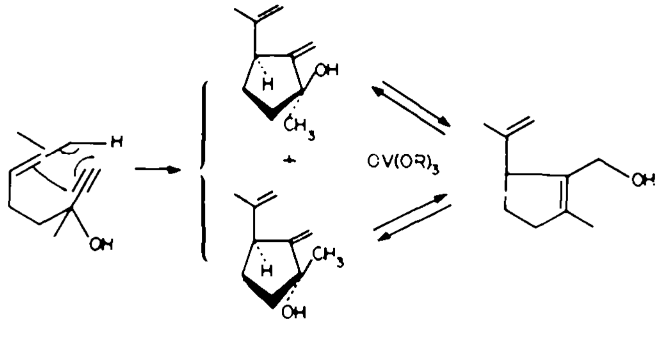
CONCLUSION

The use of oxo-metallic derivatives, especially vanadates, in isomerisation reactions of unsaturated alcohols, opened a new and faster way in the synthesis of unsaturated carbonyl derivatives and of allylic alcohols. The first industrial application of these findings is the synthesis of citral from dehydrolinalol.

EXPERIMENTAL

The vapour phase chromatography was carried out on Hewlett-Packard models F & M 720 or 5750, with a Hewlett-Packard 3380 integrator. The IR spectra were recorded on a Perkin-Elmer 237 spectrometer, using the material as a film or in Nujol. The NMR spectra were recorded on Varian T 60 or HA 100 spectrometers using TMS as an internal standard and CCl_4 as solvent.

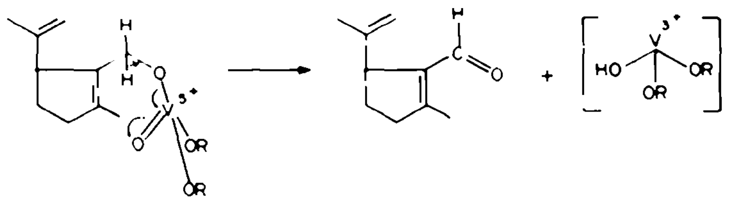
Preparation of the vanadates. This is carried out in accordance with the conventional methods in the literature, namely reaction of the alcohols with V_2O_5 (in the case of the alcohols of low b.p.) and with NH_4VO_3 (in the case of the alcohols of higher b.p.), and transesterification reactions.



Another side reaction consists of the oxidation of the alcohol to the corresponding aldehyde (the reaction scheme used in Ref. [17]). This reaction takes place, with a change in the oxidation level of the metal, in accordance with the following mechanism.

Similar cyclic mechanism is proposed[18] for oxidation of alcohols through their chromic esters.

Determination of the carbonyl products by oximation. 6–7 mmols of carbonyl product are dissolved in 80 ml of 95° strength alcohol and 20 ml of water; the pH is brought to 3.5. 20 ml of a solution, of pH 3.5, of hydroxylamine hydrochloride (50 g in 167 ml of water and 800 ml of 95° strength alcohol) are added. The reaction is allowed to take place whilst stirring (20 min in the case of citral); the mixture is returned to pH 3.5 by means of 0.5 N sodium hydroxide solution (the pH being measured).



Determination of the monosubstituted acetylenic derivatives with silver nitrate (according to S. Siggia[19]). The nitric acid resulting from the formation of silver acetylide is determined by potentiometric titration.

Determination of dehydrolinalol and of citral by vapour phase chromatography. F & M 720: column 1.8 m × 1/4 ft; 10% Apiezon on Embacel; injector and detector at 280°, and oven at 120° for dehydrolinalol and 150° for citral. Helium flow 60 ml/min F & M 5750; column 3 m × 1/8 ft; 15% UCON LB 550 X on Chromosorb W 60/80 mesh. Injector at 240°, detector at 280°, oven raised from 150° to 180° at 1°/min. Helium flow 1.8 l/h. Internal standard methylheptenone. These last-mentioned conditions make it possible to separate the following: methylheptenone, 1-hydroxy-1-methyl-2methylene-3-isopropenyl-cyclopentane (*cis* isomer, followed by *trans* isomer), dehydrolinalol, 1-isopropenyl-2-formyl-3-methyl-cyclopent-2-ene, neral, 1-isopropenyl-2-methylol-3-methyl-cyclopent-2-ene and geranial (increasing retention times)

Isomerisation experiment in the absence of a solvant. 150 g of dehydrolinalol and 0.8 g of triethanolamine orthovanadate are introduced, under an inert atmosphere, into a 500 ml flask equipped with a stirrer, a thermometer, a nitrogen inlet and a short Vigreux column. The mixture is heated to 160°C over the course of 10 min whilst stirring, and this temperature is maintained for 35 min. The homogeneous yellow reaction mixture is cooled to 60° and is rapidly distilled under 0.1 torr below 120° in the flask 150 g of dehydrolinalol are charged onto the residual mass thus obtained, and the mixture is heated for 35 min at 160°. 5 recyclings are carried out in this way. The determination of the dehydrolinalol (silver nitrate method) and of the citral (oximation) gives the following results, over all the operations carried out: yield of citral = 77% relative to the dehydrolinalol converted, degree of conversion 18%

Isomerisation experiment in a diluted medium. 20 g of dehydrolinalol, 1 g of cyclohexyl orthovanadate and 50 ml of paraffin oil are introduced, under an inert atmosphere, into a 250 ml flask equipped as above. The mixture is stirred and heated for 1 h at 125°, and the resulting dehydrolinalol/citral mixture is distilled *in vacuo* (0.1 torr) without exceeding 100° in the flask. 20 g of dehydrolinalol are charged onto the residual mass thus obtained and the mixture is heated for 1 h at 125°. 11 recyclings, involving a total of 239.3 g of dehydrolinalol, are carried out in this way. The chemical determinations of the citral formed and of the residual dehydrolinalol give, over all the operations, a yield of citral of 77% and a degree of conversion of the dehydrolinalol of 14%, representing, at this stage, a consumption of vanadium equivalent to 0.015 gram atom per molecule of citral formed

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