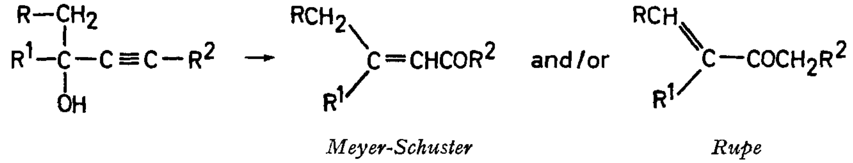
126. The Rearrangement of α-Acetylenic Alcohols to α, β-Unsaturated Carbonyl Compounds by Silylvanadate Catalysts

by **Horst Pauling**[1]), **David Arthur Andrews**[2]) and **Nathan Chadwick Hindley**[3])

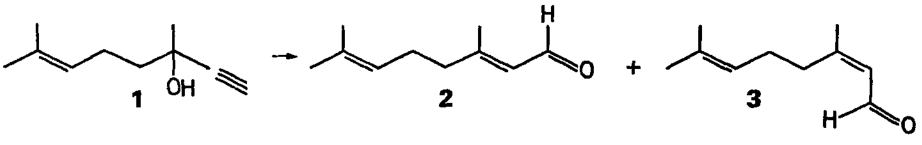
(27. II. 76)

Summary. New catalytic systems have been found which effect the isomerization of α-acetylenic alcohols to the corresponding α,β-unsaturated carbonyl compounds with high efficiency. These are combinations of silylvanadates with silanols or silanediols.

α,β-Unsaturated carbonyl compounds, important intermediates in the manufacture of fragrances [1], carotenoids, and vitamins [2] have been obtained by reactions of α-acetylenic alcohols in the *Meyer-Schuster* [3] and *Rupe* [4] type rearrangements which have been the subjects of a large number of investigations [5] [6] and some contradictory reports [7]. Such rearrangements have been achieved by the use of a wide variety of acidic reagents [5] [6] [8] which often lead to complex mixtures of products.



Rearrangements of esterified acetylenic alcohols, however, proceed in high yield in the presence of certain transition metals [9] in charge induced [3*s*,3*s*]-sigmatropic reactions [10] [11], and the intermediates saponify cleanly to α,β-unsaturated carbonyl compounds. Such a reaction has provided an important technical process for the manufacture of citral (**2** + **3**) from dehydrolinalool (**1**).



---

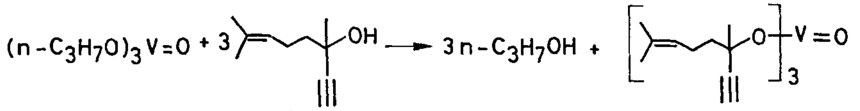
[1]) Author to whom correspondence should be addressed: Department of Vitamin and Nutritional Research, *F. Hoffmann-La Roche & Co.*, Ltd., Basel, Switzerland.

[2]) Technical Development Department, *Hoffmann-La Roche Inc.*, Nutley, New Jersey 07110, USA.

[3]) Process Research Department, *Roche Products Ltd.*, Welwyn Garden City, Hertfordshire, England.

We now report efficient procedures by which α-acetylenic alcohols may be rearranged directly by the use of silylated vanadates, particularly tris(triphenylsilyl)vanadate(V), as catalysts.

Readily available alkylvanadates, such as tri-*n*-propylvanadate (**4**) can be easily transesterified with successive replacement of the three propyl groups by dehydrolinalyl groups. The three dehydrolinalylvanadates formed (*e.g.* **5**) decompose at elevated temperatures with the formation of some citral (**2** + **3**); we obtained yields of 31–37% from reactions under a variety of conditions but many by-products formed, and the vanadate was converted to black material which was inactive in effecting further rearrangement but very active in effecting decomposition reactions of citral (cf. [12–14]). In contrast to these results, we observed [15] that dehydrolinalool is rearranged cleanly and almost completely to citral by tris(trimethylsilyl)vanadate(V) in hydrocarbon solvents at 125–140°.



4 **1** **5**

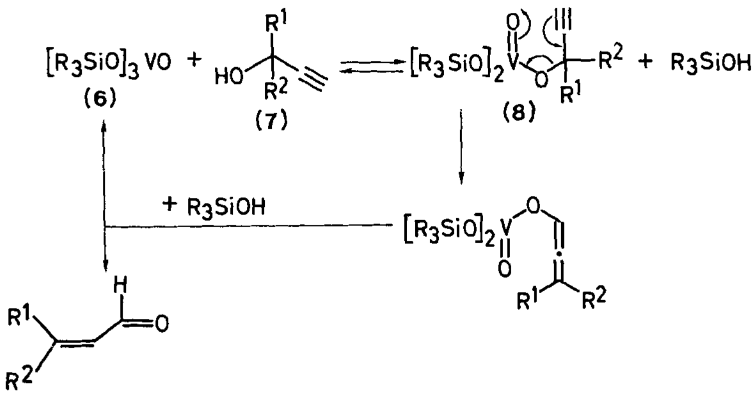
Tris(triphenylsilyl)vanadate(V) and dehydrolinalool in various solvents at 140° for 5–10 minutes gave citral in 78% yield; over 90% of the dehydrolinalool reacted, and over 90% of the silylvanadate crystallized unchanged from cooled reaction mixtures. When less than the stoichiometric proportion of tris(triphenylsilyl)vanadate(V), *e.g.* 0.1–0.05 mol per mol of dehydrolinalool, was used, the reactions became slow after 3–5 minutes at 140°; at this time 0.2–0.3 mol of citral had formed and 0.5–0.6 mol of dehydrolinalool had reacted. When such reactions were allowed to proceed, the dehydrolinalool eliminated water and the citral yields declined from a maximum. This inhibition of the rearrangement was overcome by the use of a carboxylic acid, *e.g.* 0.1–0.05 mol of lauric or benzoic acid per mol of dehydrolinalool which, in conjunction with tris(triphenylsilyl)vanadate(V), gave maximum yields of 85–90% of citral in 25–30 minutes and almost complete conversions of dehydrolinalool in 30–40 minutes. The vanadate could still be recovered by filtration but, when high-boiling solvents were used, the products were isolated more conveniently by distillation, and the cycle was repeated by adding more of the acetylenic alcohol and without isolating the catalyst.

For the rearrangement of dehydrolinalool optimum conditions were developed by conducting reactions in the presence of an excess of triphenylsilanol, although longer reaction times were needed for complete conversions, as implied, if the transesterification reaction (**6** + **7** → **8**) is rate-determining. High yields of citral could thus be maintained over a larger number of recycling experiments than for faster conversions without excess triphenylsilanol. In later cycles, however, increasing proportions of by-products reduced the yield of citral from over 90% to 82%.

A variety of tertiary α-ethynyl alcohols were rearranged by tris(triphenylsilyl)vanadate(V) with the results summarized in the experimental section4) but, with the

---

4) See also [16].



exception of dehydrolinalool and 2-methyl-3-butyn-2-ol, optimum conditions were not sought; non-terminal α-alkynols gave ketones[4]), and one of the secondary alcohols examined, namely 1-nonyn-3-ol gave two products: non-2-en-1-al by *Meyer-Schuster* rearrangement, and, in small proportion, non-3-en-2-one by *Rupe* type rearrangement.

A wide variety of silanols and their corresponding vanadates were prepared (Tables 1 and 2, see exper. part) and examined for catalytic activity. The alkylsilanols which readily form disiloxanes were less effective in recycling experiments than those, such as tricyclohexylsilanol, which do not. The latter silanol, and triarylsilanols carrying electron-donating groups in the aromatic rings formed silylvanadates which gave slower rearrangements than tris(triphenylsilyl)vanadate(V). The presence of certain electron-withdrawing groups in the aromatic rings of the arylsilyl groups, however, gave faster rearrangements, and lower temperatures became practical for the rearrangements[4]); however, we found no such silylvanadate which was as stable as tris(triphenylsilyl)vanadate(V) in recycling experiments, possibly as a result of a greater tendency to form disiloxanes.

Silanediols in conjunction with alkylvanadates formed catalysts which gave faster rearrangements than tris(triphenylsilyl)vanadate(V) but which were less stable, and their activity could not be sustained in recycling experiments.

Experimental part

General. Melting points were determined on a *Mettler* FP I and were not corrected. Spectral measurements were done by the members of the Physical Chemistry Department of *Hoffmann-La Roche* using the following instruments: NMR., *Varian* T 60 spectrometer with TMS ($\delta = 0$ ppm) as internal standard, chemical shifts are given in δ, coupling constants J in Hz; IR., *Beckmann* IR. 9 spectrophotometer, absorptions in cm^{-1}; MS., 9 (*AEI*, Manchester, England), massnumbers in *m/e*, relative intensity in % in parentheses; GLC., *Perkin-Elmer* F 20 combined with an *Infotronics* Automatic Digital Integrator Model CRS-208 working with internal standards; see also chapter 2.1.1.

1. Preparation of materials. – 1.1. *Triphenylsilanol* [17]. Silicon tetrachloride (57.6 ml, *Fluka puriss.*) and ether (4 l) in dried apparatus and under nitrogen were stirred vigorously at 3–5°, and a freshly prepared solution (600 ml) of phenyl lithium (126 g) in ether was added over 2.5–3 h. The mixture was stirred overnight at room temp. and hydrolysed below 25° by the addition of water (2 l). After neutralization to phenolphthalein with aqueous ammonia (37%, *ca.* 50 ml), separation of the ether layer and two more extractions with ether (0.5 l), the combined ether solutions were dried with sodium sulfate and decolorized by stirring with charcoal (4 g, *Darco* G 60) for 5 min. The filtered solution was evaporated and the residue dissolved in boiling ligroin (2.5 l, b.p. 80–105°). Slow cooling to 25° and refrigeration at +5° gave white crystals which were filtered off, washed with petroleum ether (200 ml, b.p. 40–45°) in several portions, and dried at 60° and 20 Torr: 124 g (90%) of triphenylsilanol, m.p. 153°. – MS.: 276 (*M*, 35), 199 ($M-C_6H_5$, 100), 122 (24), 77 (20), 95 (16). – NMR. ($CDCl_3$): 3.22 (*s*, 1H), 7.0–7.7 (*m*, 18H).

1.2. *Tris*(m-*trifluoromethylphenyl*)*silanol* [18][5]. Freshly prepared *m*-trifluoromethylphenyl lithium [17] in ether, from *m*-trifluoromethylbromobenzene (55.1 g), was added over 2–3 min to a solution of trichlorosilane (13.0 g, *Fluka*) in ether (800 ml) at –5 to 0° in dry apparatus and under nitrogen. After the mixture was stirred for 1 h, distilled water was added, the ether layer separated, washed with water until neutral, and dried over sodium sulfate. The solvent was vacuum-distilled and the residue purified by column chromatography on silica gel (200 g, *Merck* G 60); elution[6] with ligroin (b.p. 80–105°)/ether 95:5 and evaporation of the solvent gave 28.8 g (68.8%) of tris(*m*-trifluoromethylphenyl)silane. Hydrogen was evolved during the dropwise addition of a solution of this silane in ether (200 ml) to a mixture of acetone (100 ml), distilled water (10 ml), and aqueous ammonia (37%, 10 ml). The ether layer was separated, washed neutral with water, and dried over sodium sulfate. About half of the ether was vacuum-distilled and replaced with an equal volume of *n*-hexane[7]. The solvent was evaporated to leave a colorless oil (24.7 g) which was dissolved in ligroin (20 ml, b.p. 80–105°) and refrigerated overnight to obtain colorless crystals which were filtered off and dried (20°, 1 Torr, 5 h): 15.1 g (36.3%) of tris(*m*-trifluoromethylphenyl)silanol, m.p. 83–84°. Two more crops (3.05 g, m.p. 80–82°) were isolated after chromatographic purification (as above, for the silane) and recrystallization from ligroin. – MS.: 480 (*M*, 4), 461 ($M-F$, 11), 335 ($M-C_7H_4F_3$, 100), 271 (11), 252 (23), 209 (8), 183 (9), 145 (4), 126 (72).

1.3. The *miscellaneous silanols* summarized in Table 1 were prepared by standard methods [19]. Spectra consistent with structure were obtained.

Table 1. $R^1R^2R^3SiOH$[a])

R^1	R^2	R^3	Physical Constant
CH_3	CH_3	CH_3	
CH_3	CH_3	C_2H_5	
CH_3	C_2H_5	C_2H_5	
C_2H_5	C_2H_5	C_2H_5	
n—C_3H_7	n—C_3H_7	n—C_3H_7	
n—C_4H_9	n—C_4H_9	n—C_4H_9	
CH_3	CH_3	C_6H_5	
CH_3	C_6H_5	C_6H_5	
C_6H_5	C_6H_5	C_6H_5	
o—$CH_3C_6H_4$	o—$CH_3C_6H_4$	o—$CH_3C_6H_4$	
m—$CH_3C_6H_4$	m—$CH_3C_6H_4$	m—$CH_3C_6H_4$	m.p. 77–78°
p—$CH_3C_6H_4$	p—$CH_3C_6H_4$	p—$CH_3C_6H_4$	
p—$C_2H_5C_6H_4$	p—$C_2H_5C_6H_4$	p—$C_2H_5C_6H_4$	m.p. 100–101°
C_6H_{11}	C_6H_{11}	C_6H_{11}	
p—$(CH_3)_2NC_6H_4$	p—$(CH_3)_2NC_6H_4$	p—$(CH_3)_2NC_6H_4$	
p—$(CH_3)_2NC_6H_4$	p—$(CH_3)_2NC_6H_4$	C_6H_5	m.p. 125°
p—$(CH_3)_2NC_6H_4$	C_6H_5	C_6H_5	
$C_6H_5CH_2$	$C_6H_5CH_2$	$C_6H_5CH_2$	

---

[5] Preparations from $SiCl_4$ or $SiBr_4$ and the *Grignard* or lithium reagent gave only low yields (5–10%).

[6] Monitored by TLC. on precoated silicagel plates F 254 (*Merck*) with same elution mixture and detection by UV. (254 nm).

[7] Omission of this step resulted in the formation of the disiloxane.

Table 1 (continued)

R^1	R^2	R^3	Physical Constant
p—FC_6H_4	p—FC_6H_4	p—FC_6H_4	m.p. 90°
p—ClC_6H_4	p—ClC_6H_4	p—ClC_6H_4	
p—BrC_6H_4	p—BrC_6H_4	p—BrC_6H_4	m.p. 126–127°
o—$CH_3OC_6H_4$	o—$CH_3OC_6H_4$	o—$CH_3OC_6H_4$	m.p. 174°
m—$CF_3C_6H_4$	m—$CF_3C_6H_4$	m—$CF_3C_6H_4$	m.p. 82–84°
p—$CF_3C_6H_4$	p—$CF_3C_6H_4$	p—$CF_3C_6H_4$	M: 480 m/e
p—$Br(m$—$NO_2)C_6H_3$	p—$Br(m$—$NO_2)C_6H_3$	p—BrC_6H_4	m.p. 251°
1—$C_{10}H_7$[b]	1—$C_{10}H_7$[b]	1—$C_{10}H_7$	m.p. 205°
1—$C_{10}H_7$[b]	1—$C_{10}H_7$[b]	C_6H_5	M: 376 m/e
1—$C_{10}H_7$[b]	C_6H_5	C_6H_5	M: 326 m/e
p—$C_6H_5C_6H_4$	p—$C_6H_5C_6H_4$	p—$C_6H_5C_6H_4$	
i—C_3H_7	i—C_3H_7	OH	
CH_3	t—C_4H_9	OH	
CH_3	C_6H_5	OH	
C_6H_5	C_6H_5	OH	
C_6H_{11}	C_6H_{11}	OH	
$C_6H_4CH_2$	$C_6H_4CH_2$	OH	
p—$(CH_3)_2NC_6H_4$	p—$(CH_3)_2NC_6H_4$	OH	
p—ClC_6H_4	p—ClC_6H_4	OH	
p—BrC_6H_4	p—BrC_6H_4	OH	
1—$C_{10}H_7$[b]	1—$C_{10}H_7$[b]	OH	
p—$CH_3OC_4H_6$	p—$CH_3OC_6H_4$	OH	m.p. 118–121° M: 276 m/e

[a] Also $(HO)Si(C_6H_5)_2$—C_6H_4—$(C_6H_5)_2Si(OH)$, m.p. 223–225°.

[b] 1—$C_{10}H_7$ = α-Naphthyl.

1.4. *Tri-*n*-propylvanadate(V)* [20]. Vanadium pentoxide (50 g, *B.D.H.*) and 1-propanol (500 ml) were stirred at reflux, and the water formed was removed continuously by fractional distillation of the azeotrope using a column of *Fenske* helices (50 cm × 1.5 cm diameter). Dry 1-propanol (100 ml) was dropped in to maintain the original volume. After 24 h solid material (14.45 g) was filtered off with exclusion of moisture, washed with 1-propanol, and dried. Evaporation of the solvent and distillation of the residue gave tri-*n*-propylvanadate (V) (94.5 g, b.p. 100–105°/0.1 Torr) as a yellow liquid.

The still residue (1.17 g) was combined with the solid material (14.45 g) and heated at 400° for 4 h to recover vanadium pentoxide (14.5 g). Reaction of this material with 1-propanol as described above gave more tri-*n*-propylvanadate(V) (19.8 g), and a repetition of the process yielded additional tri-*n*-propylvanadate (4.7 g), in a total yield of 98%.

1.5. *Tris(trimethylsilyl)vanadate(V)* [21] [22]. A solution of chlorotrimethylsilane (85.5 ml, *Fluka*) in ether (1.05 l) was dropped into a stirred solution of pyridine (112 ml), ether (2.1 l), and water (12.6 ml) at 0°. After 10 min a solution prepared by slowly adding vanadium oxychloride (20 ml) to ether (0.7 l) cooled to 0–5° was dropped in, and, after the mixture had warmed to 20–25°, the pyridine hydrochloride was filtered off under nitrogen. The solvent was evaporated and the residue fractionally distilled with exclusion of air and moisture to obtain tris(trimethylsilyl)vanadate (44.2 g (63%), b.p. 103–105°/10 Torr) – IR.: 911 [22] [23].

1.6. *Tris(triphenylsilyl)vanadate(V)* [21] [23] [24]. 1.6.1. ***From vanadium oxide.*** Vanadium pentoxide (22.2 g, 99.5% pure), triphenylsilanol (165.8 g), butanol (44.5 g), and xylene (700 ml) were refluxed, and the water formed was removed continuously (*Dean-Stark* apparatus) during 7 h. Black material (6 g) was filtered off, washed with boiling xylene (5 × 25 ml), and dried. The combined filtrates were allowed to cool, and the crystals were filtered off, washed with xylene (2 × 25 ml) and hexane (2 × 50 ml), and dried: 138.5 g (77.2%) of tris(triphenylsilyl)vanadate(V), m.p. 225–227°. A second crop (24.8 g, 13.8% yield) was obtained by concentrating the xylene mother liquors. The first and second crops contained 0.9% and 1.2% unreacted triphenylsilanol (estimation by IR. relative to pure standards), and further purification was effected by recrystallization from benzene, xylene, or mesitylene.

1.6.2. *From vanadium oxychloride.* Solutions of pyridine (124.5 g) in benzene (1.35 l) and of vanadium oxychloride (82.5 g) in benzene (1.35 l) were added at approximately the same rate to, and beneath the surface of, a stirred solution of triphenylsilanol (414.6 g, m.p. 152–153°) in benzene (4.5 l). The additions were completed in 2.5 h, and the temp. rose from 21 to 31° without any cooling. After 3 h more, pyridine hydrochloride was filtered off and the solution concentrated to a slurry which was diluted with ether (3 l) and filtered. The crystals were washed with ether and vacuum-dried at 40–50°: 383 g (89.8%) of tris(triphenylsilyl)vanadate(V), m.p. 224–226°.

1.6.3. *From tri-*n*-propylvanadate(V)* or 1.6.4. *From tris(trimethylsilyl)vanadate(V).* Reactions between triphenylsilanol and these vanadates were carried out in dry benzene and under nitrogen by distilling out 1-propanol or trimethylsilanol with the benzene. Recrystallization of the residues from mesitylene gave tris(triphenylsilyl(vanadate(V) (m.p. 225–226°) as white crystals in yields of 92 and 88%, respectively. – IR.: 910 (V = O); 1120, 1105, 1006 (Si—O). – MS.: 897 (*M*, 65), 820 (*M* – C_6H_5, 66), 738 (11), 660 (15), 584 (45), 506 (30), 276 (22), 259 (100), 199 (52).

1.7. The *miscellaneous silylvanadates* (Table 2) used in this investigation were prepared according to methods from the literature and as described above for tris(triphenylsilyl)vanadate(V). Satisfactory analyses and spectral data consistent with the structures were obtained in all cases. Vanadium and silicon were determined by methods from the literature [24].

Table 2. *Silylvanadates*

Formula	Reference or Method [a]	Physical Constants
$[(CH_3)_2(C_2H_5)SiO]_3VO$	[21]	b.p. 124–126°/7 Torr
$[(CH_3)(C_2H_5)_2SiO]_3VO$	[21]	b.p. 169–170°/5 Torr
$[(C_2H_5)_3SiO]_3VO$	[21] [25]	b.p. 198–201°/12 Torr
$[(C_3H_7)_3SiO]_3VO$	[26]	
$[(C_6H_5)(C_2H_5)_2SiO]_3VO$	[21]	b.p. 263–268°/1.5 Torr
$[(CH_3)_3SiO]_2V(O)\text{—}OCH(CH_3)_2$		
$[(CH_3)_2CHO]_2V(O)\text{—}OSi(CH_3)_3$	[18]	b.p. 73–74°/2.5 Torr
$[(C_6H_{11})_3SiO]_3VO$	1.6.2., 1.6.3., 1.6.4.	m.p. 267°
$[(m\text{—}CH_3C_6H_4)_3SiO]_3VO$	1.6.2.	m.p. 93°
$[(p\text{—}CH_3C_6H_4)_3SiO]_3VO$	1.6.2.	m.p. 121°
$[(p\text{—}CH_3OC_6H_4)_3SiO]_3VO$	1.6.2.	m.p. 164°; *M*: 1162 *m/e*
$[(p\text{—}(CH_3)_2NC_6H_4)_3SiO]_3VO$	1.6.2.	m.p. 171°
$[(p\text{—}FC_6H_4)_3SiO]_3VO$	1.6.2.	m.p. 147°; *M*: 1054 *m/e*
$[(p\text{—}ClC_6H_4)_3SiO]_3VO$	1.6.3.	m.p. 181°; IR.: 890 cm^{-1}
$[(p\text{—}BrC_6H_4)_3SiO]_3VO$	1.6.3.	m.p. 175°; IR.: 900 cm^{-1}
$[(m\text{—}CF_3C_6H_4)_3SiO]_3VO$	1.6.3.	IR.: 917 cm^{-1}; *M*: 1504 *m/e*
$[(p\text{—}CF_3C_6H_4)_3SiO]_3VO$	1.6.3.	IR.: 920 cm^{-1}; *M*: 1504 *m/e*
$[(p\text{—}C_6H_5C_6H_4)_3SiO]_3VO$	1.6.2.	m.p. 114–116°

[a] For methods see chapter 1.6.

1.8. *Tris(3,7-dimethyl-oct-6-en-1-yn-3-yl)vanadate(V)* (= *tris(dehydrolinalyl)vanadate*) (**5**). Tri-*n*-propylvanadate (1 mol) and dehydrolinalool (1 mol) were incubated at 40° under vacuum (15 Torr), and 1-propanol (1 mol) distilled out in about 30 min. Similar treatments with a second and third mol of dehydrolinalool required 1 h and 3 h, respectively, for complete displacement of the 1-propanol and to leave tris(dehydrolinalyl)vanadate (**5**). – IR. ($CHCl_3$): 917 (V = O). – NMR. ($CDCl_3$, 60 MHz; in square brackets the corresponding values for the free dehydrolinalool): 1.63 [1.52] (*s*, H_3C—C(3)); 1.68 [1.70] (broadened by additional long-range coupling, H_3C—C(7)); 2.53 [2.47] (*s*, H—C(1)); 5.12 [5.17] (~*t*, *J* ~ 7, broadened by additional long-range coupling, H—C(6)).

2. Rearrangement reactions. – 2.1. *Quantitative determinations.* 2.1.1. *Aldehydes by oximation.* Weighed samples containing 1.5–1.7 mmol of aldehyde were treated with 2-dimethylaminoethanol (20 ml, 0.25 M in ethanol) and hydroxylamine hydrochloride (25 ml, 0.4 M in ethanol). After 1 h at room temp., the solutions were titrated (V_s in ml) with 0.2 M aqueous perchloric acid using as indicator 5 drops of a mixture of *Mauritius* yellow (0.0667 g) and methyl violet (0.004 g) in ethanol (50 ml). The same procedure was performed without the aldehyde for the blank titration (V_b in ml). Vanillin (99.9% pure by differential scanning calorimetry) was used as a standard.

$$\%\ \text{aldehyde} = \frac{(V_b - V_s) \times (\text{molarity of perchloric acid}) \times (\text{mol.-wt. of aldehyde})}{10 \times (\text{sample weight in grams})}$$

2.1.2. *Citral and dehydrolinalool by gas-liquid chromatography* (GLC.). Gas chromatograms were obtained on *Pye* 104 or *Hewlett-Packard* Model 5700 A with flame ionization detection. Glass columns: 152 × 0.64 cm or 200 × 0.4 cm; stationary phase: Apiezon L 5% or OV 225 3% on Chromosorb W, AW, DMCS, 100–120 mesh or Superceloport 100–200, at 135–150° or 110°; on-column injection; carrier gas: nitrogen (40–60 ml/min) or helium (60 ml/min); internal standards: tridecane or octadecane. Pure standards of dehydrolinalool (**1**), neral (**3**), and geranial (**2**) were obtained by fractional distillation; neral (**3**) was further purified through the bisulfite compound and geranial (**2**) by three crystallizations from petroleum ether at –100°. Programmed runs were at 8°/min, 8 min after injection, and peak areas were integrated by *Kent* Chromalog II or *Hewlett-Packard* 3370 A.

2.2. *Rearrangement of 3,7-dimethyloct-6-en-1-yn-3-ol* (= *dehydrolinalool*) (**1**). 2.2.1. *Search for optimum conditions.* Fractionally distilled dehydrolinalool (3.75 g, b.p. 40–42°/0.1–0.2 Torr, 99.2–99.4% by GLC.) in a solvent (50 ml, xylene, mesitylene, octadecane, octacosane, diphenyl ether, bis[2-(2-methoxy-ethoxy)-ethyl] ether, dibutyl phthalate or mineral oil) at the required temp (*e.g.* 140 ± 0.5°) was added to solutions or stirred suspensions of the potential catalyst in the same solvent. Samples were withdrawn periodically and analyzed by GLC.

2.2.2. *By tris(triphenylsilyl)vanadate.* 2.2.2.1. Tris(triphenylsilyl)vanadate(V) (30 g), triphenylsilanol (60 g), stearic acid (3 g), and mineral oil (2.4 l, USP grade) were heated to 150 ± 3° under nitrogen. Dehydrolinalool (90 g, 98.5% by GLC.) was added, and after 1–5 h at 150° the mixture was cooled to 70° and crude citral (b.p. 70–90°/1.5 Torr) was distilled out. The reaction was repeated 120 times by adding dehydrolinalool (∼ 90 g) after each distillation, and the reaction time was reduced to 1 h after the sixtieth cycle. Distillates were blended and analysed.

Reaction	Distillate (kg)	Citral Yield[a]	Unreacted Dehydrolinalool[a]	Neral (**3**)/ Geranial (**2**)
1– 40	3.6732	90.7	1.1	1.1
41– 80	3.6041	91	1.1	1.1
81–120	3.5285	82.4	2.0	1.05

[a] in %, by GLC.

Fractional distillation (30 × 2.5 cm, *Goodloe* packing) gave purer citral (b.p. 74–75°/1.2 Torr, 98% by GLC., yield 75%).

The cooled reaction mixture was diluted with hexane (2 l) and the solid was filtered off, washed with hexane (4 × 0.2 l), and dried: 42–4 g, m.p. 157–206°. Extraction with ether (0.2 l) and recrystallization from toluene (0.2 l) gave tris(triphenylsilyl)vanadate(V): 20.7 g (69%), m.p. 224–227°. Evaporation of the ether extract and recrystallization of the residue from toluene gave triphenylsilanol: 15.7 g (26.2%), m.p. 150–152.5°.

2.2.2.2. Tri-*n*-propylvanadate (0.25 g), triphenylsilanol (3.3 g), stearic acid (0.2 g), and dehydrolinalool (10 g, 99% by GLC.) in paraffin oil (100 ml) were heated under nitrogen to 140 ± 0.5°. After 4 h, the mixture was cooled to 70° and crude citral was distilled out at < 0.1 Torr, the last traces of volatile products being removed by heating for 30 min at 140° and by heating the distillation head. The sequence was repeated nine times by adding more dehydrolinalool

(10 g) and by reducing the reaction times to 3.75 h for cycles 4 and 5 and to 3.5 h for cycles 6–10. The combined distillates (98.5 g) contained 93–94% citral (determined by oximation and GLC.) and 3.4% unreacted dehydrolinalool (GLC.).

2.2.3. *By tris(tricyclohexylsilyl)vanadate.* Tris(tricyclohexylsilyl)vanadate(V) (5.3 g), tricyclohexylsilanol (10.6 g), stearic acid (0.5 g), and mineral oil (400 ml) were heated at 160°. Dehydrolinalool (15 g) was added and the products were distilled out after 105 min at 160 ± 3°: 14.7 g, b.p. 51–57°/0.7–0.07 Torr. The cycle was repeated 87 times by adding more dehydrolinalool (15 g) after each distillation and increasing the reaction times to 145 min after reaction No. 10. Blends of distillates No. 1–20 (304.3 g) contained 83.2% citral (by oximation), No. 21–40 (301.1 g) 83.2%, No. 41–60 (303.2 g) 72.9%, No. 61–75 (239.7 g) 62%, and No. 76–87 (118.6 g) 57.4%.

2.2.4. *By dicyclohexylsilanediol and a vanadate.* Dicyclohexylsilanediol (6 g), stearic acid (0.5 g), and mineral oil (400 ml) were degassed at 100° under vacuum. Nitrogen was admitted and tri-*n*-propylvanadate (1.05 ml) was added. Dehydrolinalool (15 g) was added at 150° and the products (13.3 g) were distilled after 90 min at 150 ± 1°. The cycle was repeated 43 times by adding dehydrolinalool (15 g) after each distillation. Blends of distillates No. 1–15 (220.2 g) contained 82.6% citral (by oximation), No. 16–30 (220.5 g) 74%, and No. 31–43 (190.9 g) 56.5%.

2.2.5. *By diphenylsilanediol and a vanadate.* Diphenylsilanediol (14.1 g) and mineral oil (960 ml) were degassed and tri-*n*-propylvanadate (3.37 g) was added under dry nitrogen. The mixture was heated to 140°, dehydrolinalool (30 g) was added, and the product (30.9 g) which was distilled out after 45 min contained 82% citral and no dehydrolinalool. Successive reactions of dehydrolinalool (30 g) at 140° for 45 min gave after each distillation products containing successively higher proportions of unreacted dehydrolinalool. A blend of the first seven distillates contained 57.7% citral.

2.2.6. *By* a)*tris[tris*(m-*trifluoromethylphenyl*)*silyl]vanadate* (an example of a triarylsilanol carrying electron-withdrawing groups), b)*tris(triphenylsilyl)vanadate, and* c)*tris[tris*(p-*dimethylaminophenyl*)*silyl]vanadate* (carrying electron-donating groups on the phenyl rings). For comparison the following experiments were run under strictly identical conditions. To each of the abovementioned catalysts a), b) and c) (1 mmol), mineral oil (85 ml), and dehydrolinalool (8.5 g) were added. These mixtures were heated to 95 ± 2° under nitrogen for 3 h. The following results were obtained (by GLC.):

Catalyst	Citral Yield (%)	Unreacted Dehydrolinalool (%)
a)	61	29
b)	23	73
c)	4	93

2.3. *Rearrangement of 2-methyl-3-butyn-2-ol.* Tris(triphenylsilyl(vanadate(V) (20 g), stearic acid (1 g), 2-methyl-3-butyn-2-ol (30 g), and mineral oil (2.4 l) were heated at 140°, and the products were distilled out after 45 min by reducing the pressure (finally to < 1 Torr). The reaction was repeated by adding more methylbutynol (30 g) and by extending the reaction time to 2 h after the ninth cycle. Blends of distillates (927 g) from 30 cycles contained 3-methyl-2-butenal (91.4%, by oximation and GLC.). The mixture was cooled to 25° and filtered to recover tris(triphenylsilyl)vanadate (18.1 g (90.5%), m.p. 218–220°) as a light-brown powder.

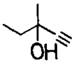
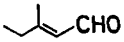
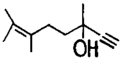
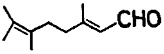
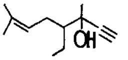
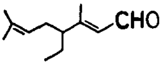
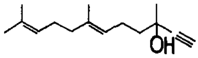
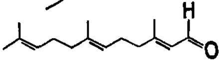
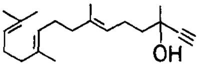
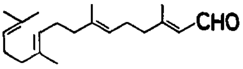
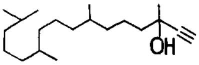
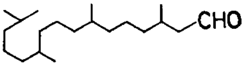
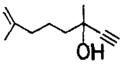
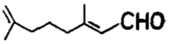
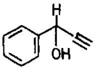
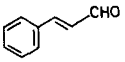
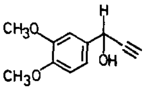
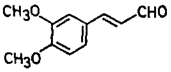
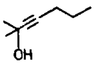
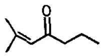
Fractional distillation gave purer (98.5% by GLC.) 3-methyl-2-butenal (also called prenal or senecioic aldehyde): b.p. 133°/730 Torr. – IR. (liquid): 1684 (ν(C=O)). – NMR. (CDCl$_3$, 60 MHz): 1.96 (*d*, *J* = 1, CH$_3$); 2.16 (*d*, *J* = 1, CH$_3$); 5.88 (*d*, *J* = 8, additional long-range coupling, H–C(2)); 9.93 (*d*, *J* = 8, H–C(1)).

2.4. *Rearrangement of 3,7-dimethyl-7-methoxy-oct-1-yn-3-ol.* Tris(triphenylsilyl)vanadate(V) (5 g), triphenylsilanol (10 g), benzoic acid (0.5 g), mineral oil (460 ml), and 3,7-dimethyl-7-methoxy-oct-1-yn-3-ol (38 g) were heated for 4 h at 140° and distilled (b.p. 64–66°/0.1 Torr). The reaction was repeated 4 times by adding more α-ethynyl alcohol (38 g) after each distillation. The cooled mixture was diluted with hexane and filtered to recover the catalyst (9.3 g, 62%).

The blend of 5 distillates (179.3 g) contained 3,7-dimethyl-7-methoxy-oct-2-en-al (93% by oximation and GLC.). – IR. (liquid): 1680 (ν(C=O)); 845, 861, 1615, 1633 (C=C); 1086 (ν(C—O—C)). – NMR. ($CDCl_3$, *cis/trans* ~0.9): 1.13 (*s*, 2 H_3C—C(7)); 1.97 (*d*, *J* = 1, H_3C—C(3) (*cis*)); 2.17 (*d*, *J* = 1, H_3C—C(3) (*trans*)); 3.15 (*s*, OCH_3); 5.90 (*d*, *J* = 8.5, broadened by additional long-range coupling, H—C(2)); 9.95 (*d*, *J* = 8.5, CHO (*cis*)); 10.00 (*d*, *J* = 8.5, CHO (*trans*)).

2.5. *Rearrangement of 3,7,11,15-tetramethyl-hexadeca-6,10,14-trien-1-yn-3-ol* (**9**) (*cf.* Table 3). Tris(triphenylsilyl(vanadate(V) (6.5 g), benzoic acid (0.5 g), and geranyldehydrolinalool (**9**) (75 g) in xylene (500 ml) were boiled under reflux for 45 min. The solvent was evaporated under reduced pressure and the residue extracted with hexane (400 ml) to leave unchanged tris(triphenylsilyl)-vanadate(V) (5.6 g, m.p. 223–226°). The solvent was again evaporated and the residue (75.9 g, 77.9% aldehyde by oximation) was distilled to obtain geranylcitral (**10**) (55% yield, b.p. 145–149°/0.25 Torr).

Table 3

Ethynyl Alcohol	Product	Cycles	Cumulative, Material Balance[a])	Aldehyde[a])	Unreacted Alcohol[a])	*Cis/Trans*[b])	$\nu_{(max)}$[c])	
							C=O	C=C
		2	90	95	2.5	0.5	1679	1636 1614
		3	97	95	2	0.84–1	1675	1630 1610
		3	91	85	1	1.2–1.4	1675	1630 1610
		2	100[d])	85	< 1	1.0	1675	1630 1610
 (**9**)	 (**10**)	3	97.6[d])	85	1	–	1680	1630 1610
		2	100[d])	86	1	–	1675	1630 1615
		1	96	92	3.5	–	1676	1634
		1	95	93	2	–	1686	1627
		1[e])	93	87	0	–	1675	1624
		1[f])	98	92	5	–	1696	1632

---

[a]) In %.

[b]) It was assumed that the low retention time peak was the *cis*-isomer.

[c]) In cm^{-1}

[d]) Contains $(C_6H_5)_3SiOH$ which distilled with the product. Solvent was vacuum pump oil.

[e]) At 125° in xylene with $[(C_6H_5)_3SiO]_3VO$ for 1 h, no $(C_6H_5)_3SiOH$ was used.

[f]) At 125° with $[(C_6H_5)_3SiO]_3VO$, no $(C_6H_5)_3SiOH$ was used.

2.6. *Rearrangement of 2,5-Dimethyl-3-hexyne-2,5-diol.* Tris(triphenylsilyl)vanadate(V) (2.5 g), triphenylsilanol (5 g), benzoic acid (0.2 g), mineral oil (230 ml), and 2,5-dimethyl-3-hexyne-2,5-diol (15 g) were heated at 140° for 4 h, cooled to 70°, and distilled (b.p. 22–40°/0.2 Torr). The reaction was repeated twice by adding more 2,5-dimethyl-3-hexyne-2,5-diol (15 g) and the catalyst mixture (6.4 g, 85.3%) was recovered as described above. The three distillates (40.9 g) were blended and fractionally distilled to obtain pure 2-hydroxy-2,5-dimethyl-hex-4-en-3-one. – IR. (liquid): 3400 (ν(OH)), 1680 (ν(C=O)), 1625 (ν(C=C)). – NMR. (neat): 1.33 (*s*, 6H); 2.00 (*s*, 3H); 2.21 (*s*, 3H); 4.33 (*s*, 1H); 6.52 (*m*, 1H).

2.7. *Rearrangement of 1-Ethynylcyclohexanol.* Under the conditions described above in 2.4., about 80% (by GLC.) of 1-ethynylcyclohexanol (25 g) reacted to give a mixture (21.3 g) of cyclohexylidene-acetaldehyde and cyclohexenyl-acetaldehyde in the proportion of 2:3. A second cycle gave similar results and the catalyst mixture was recoverd (13.1 g, 87.3%).

2.8. *Rearrangement of 1-Nonyn-3-ol.* Under the conditions described in 2.4. about 60% (by GLC.) of 1-nonyn-3-ol (29.6 g) reacted to give a mixture (22.8 g) of non-2-en-al and non-3-en-2-one in the proportion of 94:6. Two more cycles gave similar results and the catalyst mixture was recovered (13 g, 86.7%).

2.9. *Rearrangement of Miscellaneous Ethynyl Alcohols.* Under the conditions described above in 2.4., the ethynyl alcohols in Table 3 were rearranged to the corresponding unsaturated carbonyl compounds.

REFERENCES

[1] *W. Hoffmann*, Chem. Ztg. *97*, 23 (1973).

[2] *H. Mayer & O. Isler*, 'Carotenoids', Birkhaeuser Verlag, Basle 1971, p. 325.

[3] *K. H. Meyer & K. Schuster*, Ber. deutsch. chem. Ges. *55*, 819 (1922).

[4] *H. Rupe & E. Kambli*, Helv. *9*, 672 (1926); see also [5].

[5] *S. Swaminathan & K. V. Narayanan*, Chem. Rev. *71*, 429 (1971).

[6] *D. Dieterich*, in «Methoden der organischen Chemie», Houben-Weyl, 1973, Band 7/2a, p. 907.

[7] *A. W. Johnson*, 'The Chemistry of Acetylenic Compounds', Ed. Arnold & Co., London 1946, Vol. I, pp. 127–130; *F. G. Fischer & K. Loewenberg*, Liebig's Ann. Chem. 475, 183 (1929); *C. D. Hurd & R. E. Christ*, J. Amer. chem. Soc. *59*, 118 (1937); *T. Takeshima*, ibid. *75*, 3309 (1953).

[8] *G. Ohloff, V. Rautenstrauch & K. H. Schulte-Elte*, Helv. *56*, 1503 (1973); *S. Isoe, S. Katsumura & T. Sakan*, ibid. *56*, 1514 (1973).

[9] *G. Saucy, R. Marbet, H. Lindlar & O. Isler*, Helv. *42*, 1945 (1959).

[10] *H. Schlossarczyk, W. Sieber, M. Hesse, H.-J. Hansen & H. Schmid*, Helv. *56*, 875 (1973).

[11] *U. Widmer, J. Zsindely, H.-J. Hansen & H. Schmid*, Helv. *56*, 75 (1973); *M. Schmid, H.-J. Hansen & H. Schmid*, ibid. *56*, 105 (1973).

[12] *P. Chabardes & Y. Querou* (to *Rhône-Poulenc S.A.*), Brit. Pat. 1, 204, 754 (September 27, 1968).

[13] *N. C. Hindley, G. M. Leeder, T. C. Ray, R. J. E. Talbot & M. T. Vickerey*, unpublished results.

[14] *K.-J. Ploner*, unpublished results.

[15] Preliminary Communication: *H. Pauling*, Chimia *27*, 383 (1973).

[16] *G. L. Olson, H. C. Cheung, K. D. Morgan, R. Borer & G. Saucy*, Helv. *59*, 567 (1976); *G. L. Olson, K. D. Morgan & G. Saucy*, Synthesis *1976*, 25.

[17] *H. Gilman, A. G. Brook & L. S. Miller*, J. Amer. chem. Soc .*75*, 3757 (1953).

[18] *Yasuaki Nakaido & Harno Oashi*, Kogyo Kagaku Zasshi *68*, 2438 (1965); Chem. Abstr. *64*, 12712c (1966).

[19] *V. Bazant, V. Chvalovsky & J. Rathousky*, 'Organosilicon Compounds' (3 vol.), Academic Press, New York 1965.

[20] *W. Prandtl & L. Hess*, Z. anorg. Chem. *82*, 103 (1913).

[21] *N. F. Orlov, B. N. Dolgov & M. G. Voronkov*, Dokl. Akad. Nauk SSSR *122*, 246 (1958); Chem. Abstr. *53*, 2076a (1959); *N. F. Orlov, B. N. Dolgov & M. G. Voronkov*, Chim. i Prakt. Primenenie Kremneorg. Soedinenii, Trudy Konf., Leningrad *1958*, Nr. 1, 161–169; Chem. Abstr. *54*, 4360a (1960); *N. F. Orlov & M. G. Voronkov*, USSR Pat. 112,939 (August 15, 1958);

Chem. Abstr. *53*, 5131d (1959); *N. F. Orlov, B. N. Dolgov & M. G. Voronkov*, USSR Pat. 117, 658 (February 6, 1959); Chem. Abstr. *53*, 19975i (1959).

[22] *M. Schmid & H. Schmidbaur*, Angew. Chem. *71*, 220 (1959).

[23] *F. E. Granchelli, G. B. Walker*, U.S. Pat. 2, 863, 591 (December 9, 1958); Chem. Abstr. *53*, 9147i (1959).

[24] *M. M. Chamberlain, G. Kern, G. A. Jabs, D. Germanas, A. Greene, K. Brain & B. B. Wayland*, U.S. Dept. Com., Office Tech. Serv., PB Rept. 152, 086 (1960); Chem. Abstr. *58*, 2508d (1963); *M. M. Chamberlain, G. A. Jabs & B. B. Wayland*, J. org. Chemistry *27*, 3321 (1962); *M. M. Chamberlain*, AD 601.415 (1964); Chem. Abstr. *62*, 1311f (1965).

[25] *K. A. Adrianov, A. A. Zhdanov & E. A. Kashutina*, Dokl. Akad. Nauk. SSSR *126*, 1261 (959); Chem. Abstr. *53*, 21624i (1959).

[26] *S. Sekiguchi & A. Kurihara*, Kogyo Kagaku Zasshi *72* (3), 761 (1969); Chem. Abstr. *71*, 61820e (1969).

---

127. A Photo-initiated *Wagner-Meerwein* Rearrangement

Preliminary communication

by **Alan F. Thomas** and **Michel Ozainne**

Firmenich SA, Research Department, 1211 Geneva 8

(14. IV. 76)

Summary. Irradiation of the octalin-derived sesquiterpene oxide α-agarofuran in methanol leads to rearrangement to the perhydroazulene system, in addition to simple double-bond migration to β-agarofuran. This rearrangement apparently proceeds through a carbonium-ion-like intermediate, whereas conventional generation of a carbocation leads only to opening of the oxide ring without rearrangement.

α-Agarofuran (**1**) is converted into the exocyclic alkene β-agarofuran (**2**) in moderate yield by irradiation in isopropyl alcohol with xylene as sensitizer [1]. Using methanol instead of isopropyl alcohol we isolated in addition, the acetal **3** and the related hydroxy-keton **4**. The structure of the latter was established as follows. All four methyl groups were attached to quaternary carbon atoms (NMR.), and the presence of a hydrogen-bridged hydroxy-keton system was shown by bands in the IR. spectrum¹) at 3610 (free OH), 3470 (bonded OH), and 1680 cm^{-1} (bonded C=O). The position of the isopropyl group with respect to the carbonyl group was provided by a fortuitous dehydration that occurred on one occasion when compound **4** was injected onto an OV-17 gas chromatography column that had become acid with long use. Of the two substances recovered from the column, one (**5**) had a ^{1}H-NMR. spectrum²) showing the presence of only two quaternary methyl groups (0.96 and 1.09 ppm), two methyl groups on a double bond (1.71 ppm), and a methylene group between two double bonds (*AB* system, 3.08 and 3.45 ppm, $J = 15$ Hz). The other dehydration product (**6**) had the same two quaternary methyl groups (1.04 and 1.16 ppm) and an isopropenyl group (1.76 and 4.77 ppm). The acetal **3** had a ^{1}H-NMR. spectrum with five methyl groups (1.13, 1.16, 1.24, 1.36, and 3.30 ppm) and a single

---

1) IR. spectra are measured in $CHCl_3$ solution.

2) ^{1}H-NMR. spectra are measured in $CDCl_3$ solution on a *Bruker* HX-90 instrument.