Continuous Allylic Isomerization of Tertiary Vinyl Carbinols

to Compounds with Varied Odors

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Tertiary alkenols derived from the corresponding acetylenic alcohols by semihydrogenation have been isomerized in a continuous cyclical system to the corresponding allylic alcohols in yields and conversion up to 72 and 59%, respectively. Alkenols used successfully as starting materials were 3-methyl-1-buten-3-ol, 3-methyl-1-penten-3-ol, and 3,5-dimethyl-1-hexen-3-ol. Batch or noncontinuous isomerization gave conversions of only 10–11% with yields of about 25–30%. Byproducts resulting from the isomerization process were dienes, ethers, and high boiling polycondensation products. The odor characteristics of several products derived from 3-methyl-1-buten-3-ol and 3-methyl-1-penten-3-ol are summarized.

The acid-catalyzed isomerization of tertiary vinyl carbinols is an anionotropic rearrangement of which the following reactions, as shown in Figure 1, are typical.

Reaction (a), the Carrol reaction (Carrol, 1940a,b, 1941; Kimel, 1953, 1957), is a high yield rearrangement process which is commercially utilized in the preparation of perfumery compounds and vitamins A and E. The related Meyer–Schuster (b) (Bergman, 1951) and allylic (c) (Raphael, 1955; Nazarov, 1946) rearrangements, while of potential commercial utility, proceed in substantially lower yields and result in mixtures of products.

We observed (Tedeschi, 1967) that when reaction (c) was carried out batchwise using tertiary alkenols such as 3-methyl-1-buten-3-ol (MBe) and 3-methyl-1-penten-3-ol (MPe), with the acid form of Dowex 50 resin as catalyst, low conversions (11–14%) and yields (25–30%) to the desired allylic alcohol resulted. Major byproducts of the reaction were dienes, unsaturated ethers and polycondensation products. Additional batch studies with other catalysts such as boron trifluoride etherate, aluminum and zinc chlorides, sulfuric, phosphoric and formic acids also gave inferior results.

Subsequent studies showed that if the allylic rearrangement were run in a continuous system (Tedeschi, 1967; Tedeschi et al., 1971) whereby the higher boiling allylic alcohol, after emerging from the isomerization chamber, was separated from the starting alkenol, markedly improved conversions and yields were possible.

Figure 2 illustrates the mixture of products which result from the rearrangement of 3-methyl-1-buten-3-ol. Allylic alcohol (B), above 60° C, is unstable in the presence of acidic catalysts and reverts back to the tertiary alkenol (A) and eventually to isoprene (E). The allylic alcohol in turn can form a mixture of ethers, either the diallylic (C) or mixed tertiary–allylic (D) types which have been isolated from the reaction mixture. Dimethyl allyl ethers (G) may also be formed in small amount, although complete proof for their

presence has not been established to date. High boiling byproducts (H) are believed derived primarily from the allylic alcohol and unsaturated ethers. Although isoprene can be dimerized to the terpene limonene, its presence was not detected in the Dowex-catalyzed isomerization mixture.

MATERIALS AND METHODS

Continuous Isomerization System. The reaction system developed for continuous isomerization is shown in Figure 3.

The apparatus consists of a heated fractionation column (A), half-filled with Podbelniak packing (equivalent to 20 theoretical plates), condensers (B and C), a stirred and heated isomerization chamber with a fritted glass botom (D), a flow regulator (E), a pressure head and return line (F), and water separator (G). By use of an automatic temperature controller (I) and by the regulation of cooling water, the temperature in the reactor can readily be controlled to within several degrees. Since the allylic alcohol, on average, boils 50° higher than the alkenol, it is collected in the boiler (H) while starting material is recirculated. Volatile byproducts, such as isoprene, are collected in a dry ice trap (J). Soda ash or potassium carbonate is used as an acid acceptor in the boiler (H) to prevent further isomerization from traces of acid derived from the resin.

By adjusting the boil-up rate so that feed rates through the reactor average 3–7 cm³ per min, isomerizations can reach the 30–60% conversion level with respect to allylic alcohol in about 9–24 hr. The more polar and lower boiling MBe and MPe can be rearranged at atmospheric pressure, while a higher boiling alkenol such as 3,5-dimethyl-1-hexen-3-ol is preferentially handled under vacuum at 105–130° C at 100 mm (boiling point at B), prior to cooling to the reaction temperature (D) of 50–60° C.

Isomerization of 3-Methyl-1-buten-3-ol. Into the boiler (H) is charged 5.0 mol of tertiary vinyl carbinol (430 g of methyl butenol, or 500 g of methyl pentenol) and 5 g of Na_2CO_3 or K_2CO_3. The joints of the boiler are lubricated with silicone grease, sealed, and then coated with glyptal resin cement which is allowed to harden overnight. The isomerization

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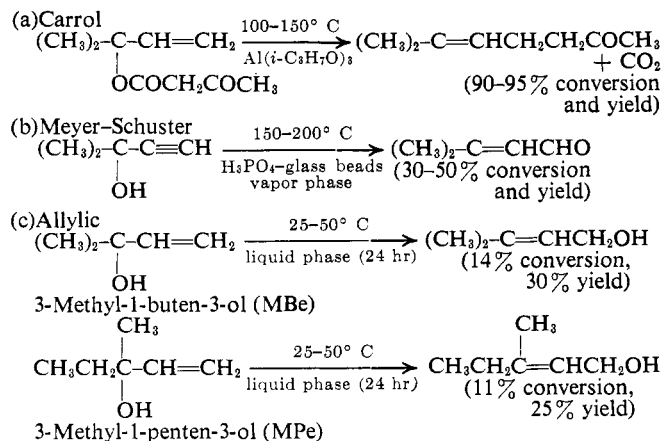Air Products and Chemicals, Inc., Middlesex, New Jersey.

(a)Carrol

$(CH_3)_2$-C-CH=CH$_2$ $\xrightarrow[Al(i-C_3H_7O)_3]{100-150° C}$ $(CH_3)_2$-C=CHCH$_2$CH$_2$COCH$_3$
|
OCOCH$_2$COCH$_3$ $+ CO_2$
(90-95% conversion and yield)

(b)Meyer-Schuster

$(CH_3)_2$-C-C≡CH $\xrightarrow[\substack{H_3PO_4-glass\ beads\\ vapor\ phase}]{150-200° C}$ $(CH_3)_2$-C=CHCHO
|
OH
(30-50% conversion and yield)

(c)Allylic

$(CH_3)_2$-C-CH=CH$_2$ $\xrightarrow[liquid\ phase\ (24\ hr)]{25-50° C}$ $(CH_3)_2$-C=CHCH$_2$OH
|
OH
(14% conversion, 30% yield)

3-Methyl-1-buten-3-ol (MBe)

CH$_3$
|
CH$_3$CH$_2$C-CH=CH$_2$ $\xrightarrow[liquid\ phase\ (24\ hr)]{25-50° C}$ CH$_3$CH$_2$C=CHCH$_2$OH
|
OH
(11% conversion, 25% yield)

CH$_3$
|
3-Methyl-1-penten-3-ol (MPe)

Figure 1. Anionotropic rearrangements

chamber (D) is charged with 5 g of Dowex-50 resin (acid form, X-1 grade, 90% H$_2$O).

The vinyl carbinol is then boiled vigorously up through the column (A) which is kept at a Variac reading of 20–30 V lower than the pot setting. With the exit stopcock (D) closed, and the stirrer of the isomerization chamber turned off, distillate is collected until the chamber is approximately half full. The stirrer is then turned on at a speed sufficient to stir the resin, but also to prevent its spattering on the wall above the liquid level.

Stopcocks (D and E) and boiling rate are now adjusted to maintain the isomerization chamber half-full of distillate while the partly isomerized effluent is returned continuously to the distillation pot. The "Temperature Guardsman" is set at a temperature of 55° C and the thermocouple (iron-constantin) protected with a suitable pyrex well inserted below the liquid level. By occasionally using the condenser (C) as a precooler, the isomerization temperature can be kept fairly constant even at higher flow rates (>7 cm³/min) through the reactor. Excess water is occasionally removed from the system via the separator (G).

As the isomerization proceeds and higher boiling allylic alcohol and byproducts are formed, the pot temperature

first drops and then gradually rises. In the isomerization of methyl butenol, the pot temperature is observed to drop from 96 to 85° C during the first hour which is probably due to the formation of the methyl butenol–water azeotrope. After 5 hr, the pot temperature climbs to 110 to 125° C depending upon the flow rate through the bed. At a flow rate of 3–7 cm³ per min through the reactor, the pot temperature reaches a value of 145–150° C during a 12-hr cycle which represents approximately a 50% conversion to allylic alcohol.

The Dowex resin in individual runs was washed with either hexane (methyl butenol) or pentane (other higher vinyl carbinols) to facilitate isolation and combined with the pot contents. A convenient way of flushing the apparatus was to place 300–400 cm³ of hexane or pentane in the still pot and continuously distil this low boiler through the system for about 30 min.

The isomerization mixture is then distilled at atmospheric pressure to remove solvent and low boilers and finally under diminished pressure to yield the corresponding allylic alcohols and ethers (cf. Table I).

DIALLYLIC ETHER (BIS-γ,γ-DIMETHYLALLYL ETHER) 3-METHYL-1-CHLORO-2-BUTENE. To 430 g (5.0 mol) of 3-methyl-1-buten-3-ol in a 1-l. stirred reactor (equipped with gas inlet and outlet tubes) at 0–5° C was added gradually anhydrous HCl gas over 75 min. The HCl was weighed into the reactor by difference from a small tank mounted on a platform balance. A total of 5.1 mol of HCl was added. The addition was exothermic and a cooling bath at −15 to −20° C was required to maintain the reaction temperature at 0 to 10° C. At the completion of the HCl addition, the reaction mixture was composed of a light orange upper layer and an aqueous HCl bottom layer.

The reaction was stirred an additional 2 hr after HCl addition was complete, and then the layers were separated. The organic layer was washed twice with cold (5° C) 10% sodium bicarbonate solution and then twice with water.

The crude product was diluted with 100 ml of hexane, and then azeotropically distilled under a Dean–Stark tube to remove water. After removal of hexane up to a pot temperature of 75° C, the product was vacuum distilled at 61–
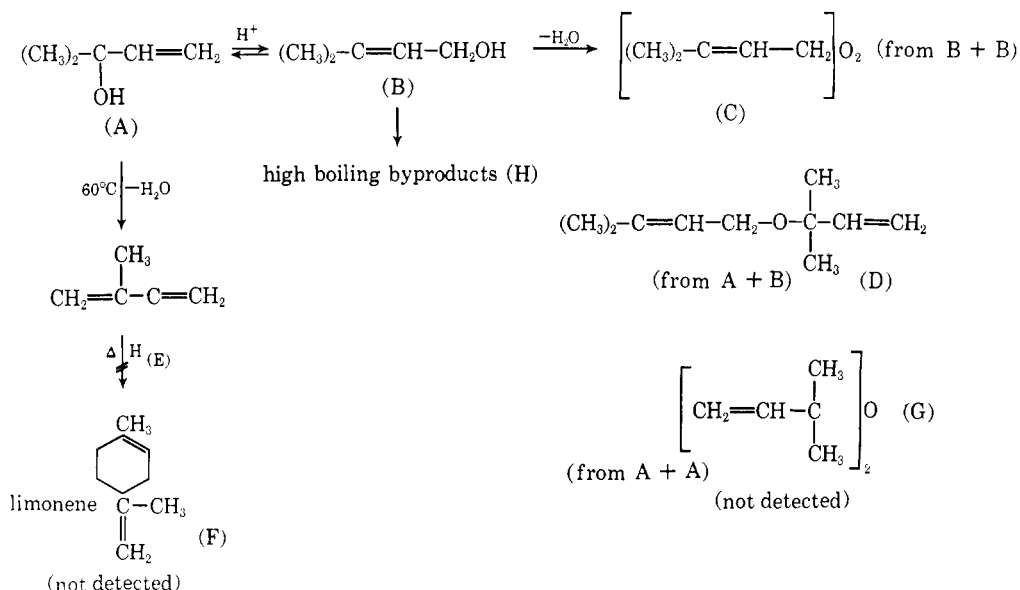
$(CH_3)_2$-C-CH=CH$_2$ $\overset{H^+}{\rightleftharpoons}$ $(CH_3)_2$-C=CH-CH$_2$OH $\xrightarrow{-H_2O}$ $\left[(CH_3)_2\text{-C}=CH\text{-}CH_2\right]O_2$ (from B + B)
|
OH
(A)

(B)

(C)

↓ high boiling byproducts (H)

60°C ↓ −H$_2$O

CH$_3$
|
CH$_2$=C-C=CH$_2$

CH$_3$
|
$(CH_3)_2$-C=CH-CH$_2$-O-C-CH=CH$_2$
|
CH$_3$
(from A + B) (D)

Δ ↓ H (E)

CH$_3$

limonene (F)
(not detected)

CH$_3$
|
$\left[CH_2\text{=}CH\text{-}C\right]O$ (G)
|
CH$_3$ ₂
(from A + A)
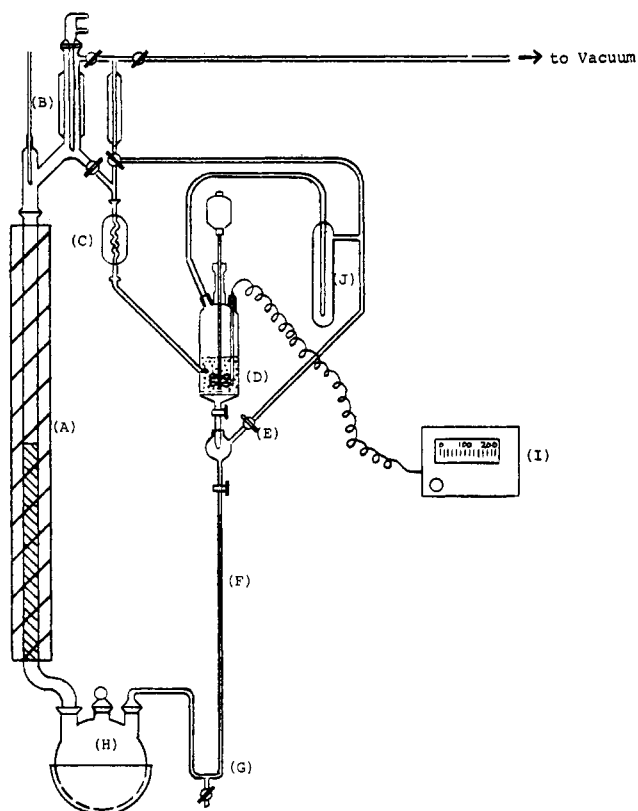(not detected)

Figure 2. Products of allylic isomerization

Figure 3. Continuous isomerization system

63° C and 150 mm (yield, 315 g of 3-methyl-1-chloro-2-butene, 60% of theory).

BIS-γ,γ-DIMETHYLALLYL ETHER. To 172 g (2.0 mol) of 3-methyl-2-buten-1-ol, well-stirred in a 1-l. reactor at 25° C, was added 68 g (1.1 mol, 61.5 g) of 90% powdered potassium hydroxide. A reaction exotherm was noted on addition of the base, with the formation of a brown slurry.

To the reaction mixture at 50–55° C was added gradually during 4 hr 104.5 g (1.0 mol) of γ,γ-dimethylallyl chloride (3-methyl-1-chloro-2-butene). The slurry gradually lightened

from a deep brown to a light yellow color with the formation of fine white crystals of KCl.

The reaction was stirred overnight at 75–80° C and the next day, after dilution with 100 ml of hexane, it was filtered from KCl. After removal of hexane, excess 3-methyl-2-buten-1-ol (87 g) was recovered by vacuum distillation at 80–82%° C/90 mm. The diallylic ether (129 g, 84% yield) was collected at 86° C/24 mm (bp 189–191° C/760 mm).

MIXED ALLYLIC–TERTIARY VINYL ETHER (γ,γ-DIMETHYL-ALLYL α,α-DIMETHYLALLYL ETHER). To 172 g (2.0 mol) of 3-methyl-1-buten-3-ol in a stirred 1-l. reactor at 0° C was added quickly 68 g (1.1 mol, 61.5 g) of 90% powdered potassium hydroxide. The resulting slurry, after having been stirred 10 min, was heated to 50° C and then treated gradually with 104.5 g (1.0 mol) of γ,γ-dimethylallyl chloride during 3 hr while raising the reaction temperature to 75–80° C. The reaction was stirred overnight and then worked up using the method of the bis-γ,γ-dimethylallyl ether. The fraction (67 g) boiling at 72–80° C/24 mm was refractionated at atmospheric pressure to yield 32 g of γ,γ-dimethylallyl-α,α-dimethylallyl ether 169–171° C (yield 44% on crude ether)

RESULTS AND DISCUSSION

Continuous Isomerization. Table I summarizes reaction conditions and average yield data obtained from the continuous isomerization of four alkenols. Conversions and yields are based on isolated products separated by fractional distillation. The following conclusions were reached from a series of runs using the continuous system.

1. Continuous isomerization was superior to a batch process by a factor of 5–6, in terms of the desired allylic alcohols.

2. The most efficient catalyst evaluated was Dowex 50 resin (acid form X-1), 50–100 mesh material, used as a wet paste containing 90% water. The use of lower mesh material or dry resin resulted in a slower rate of isomerization and lower allylic alcohol conversions. Dehydration of wet resin via the water separator, in turn increased the formation of ether byproducts to the 24–26% conversion level, showing that significant amounts of these pleasant smelling materials could be readily obtained if desired.

3. Over 4600 g of 3-methyl-2-buten-1-ol (prenol) can be

Table I. Average Data from Continuous Isomerizations

Catalyst: Dowex 50 (X-1), containing 90% H₂O. Temperature: optimum 50–55° C

	Allylic alcohols	bp	mm	Conversion	Reaction time, hr	Yield
(a)	3-Methyl-2-buten-1-ol	140–142	760	50–59	9–12	60–72
		87	100			
(b)	3-Methyl-2-penten-1-ol	98–100	100	34–50	18–26	53–61
(c)	3,5-Dimethyl-2-hexen-1-ol (DHe)	126–127	100	39–46		43–61
(d)	1-Vinylcyclohexanol	120–125	50	2.9	>27	

Dienes		Byproducts			
(a)	Isoprene	30–35	760	<1	
(b)	3-Methyl-1,3-pentadiene	60–70	760	~6	
(c)	3,5-Dimethyl-1,3-hexadiene	50–60	100	~5	

Isomeric ethers			
(a)	169–191	760	9
(b)	125–130	50	14
(c)	90–100	2	8

High boiling condensation products

(Weight percent of starting material)
MBe, 7%; MPe, 3%; DHe, 11%

Table II. Ether Byproducts of Allylic Isomerization

Ethers from 3-methyl-1-buten-3-ol (bp 70-96° C/25 mm)

	bp 760 mm	n^{20}D
1. Crude ether fraction, bp 72-76° C/25 mm	(a) 167-169	1.4408
	(b) 170-171	1.4408
2. Crude ether fraction, bp 92-95° C/25 mm	(c) 182-184	1.4510
	(d) 189-191	1.4514

Analytical values

Fraction	% element			Glc % ether	Br$_2$ value
	C	H	O		
(a)	78.0	11.60	10.50	90	93
(b)	77.8	10.80	10.81	91	93
(c)				74	76
(d)	78.1	11.75	11.12	93	99
$C_{10}H_{18}O$ (calcd) (isomeric ethers)	77.8	11.68	10.38		

Ir analysis

(a) and (b), essentially identical by ir; no OH (3200-3500 cm^{-1}) external CH_2=C present (990 cm^{-1}).

(c) and (d), very similar by ir; OH present, greatest in (c), weak in (d), external CH_2=C-absent.

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formed per gram of active resin, making for high catalyst efficiency.

4. The optimum reaction temperature appears to be 50–60° C. At higher temperatures, significant dehydration to dienes and ethers takes place.

Ether Byproducts. Crude ether distillation cuts from the rearrangement of methyl butenol (MBe) were purified by refractionation at atmospheric pressure (40 plates) and analyzed as shown in Table II.

Combustion, glc, and bromination analyses show that ether fractions (a–d) of over 90% purity can be obtained. Fractions (a) and (b) were essentially identical by ir and nmr analyses and contained both external and internal double bonds. Fraction (d) contained only disubstituted internal double bonds.

Nmr data summarized in Table III show that the lower boiling ether fractions, (a) and (b), are identical and consist of the mixed tertiary vinyl–allylic ether. The high boiling ether (d), in turn, proved to be the diallylic ether. No evidence could be found that the dimethylallyl ether (G, Figure 2) was present in any of the fractions studied. The proton ratios and chemical shifts observed clearly support the assigned structures.

The identity of the ethers (Tedeschi et al., 1971) was further confirmed by synthesis, as shown in Figure 4. The diallylic

compound (bp 189-191° C) was identical (ir, nmr, bp) with ether isolated from the isomerization mixture. Similar results were obtained in the synthesis of the allylic–tertiary vinyl isomer. An attempt to form the dimethylallyl ether (Figure 2, G) yielded a crude mixture in low yield, from which only the mixed ether (bp 167-169° C) could be isolated. This result supports the nmr data which also failed to confirm the presence of this ether (G).

High Boiling Byproducts. The identity of the high boiling byproducts remaining after separation of the isomeric ethers represents a more complex problem. Two routes to explain the formation of high boiling, polyhydroxy compounds are outlined in Figure 5. The products proposed are derived from the interaction of the dimethylallyl carbonium ion [$(CH_3)_2C$⸺$\overset{+}{C}H$⸺CH_2] with either the diallylic ether (1) of the mixed allylic–tertiary vinyl ether (2) to yield dihydroxy unsaturated ethers (3), (4), and (5). A related structure (6) is excluded by the nmr data.

Two fractions, about half of a total of 12, and boiling at 134-137° C at 2 mm, were found to be essentially identical by ir and nmr. The ir spectrum showed strong hydroxyl absorption at 3500 cm^{-1}, the presence of internal double bond at 1680 cm^{-1}, and carbon–oxygen functionality at 1070 cm^{-1}.

Table III. Isomeric Methyl Butenol Ethers. Nmr Data Chemical Shifts (ppm) (cf. Table II)

Group	(a) and (b)	(d) 189-191°C
H_2C=C (external)	4.9-6.1	0
CH_2O-	5.23	5.27
-C=C(CH_3)$_2$	1.65	1.66
>C(CH_3)$_2$	1.22	0
CH_2,CH	3.74	3.83
OH	0	0

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_2O-\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2$$ (mixed, tertiary vinyl–allylic ether)

(a) and (b)

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2OCH_2CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3$$ (diallylic ether)

(d)

Diallylic

$(CH_3)_2\overset{|}{\underset{OH}{C}}-CH=CH_2$ + HCl $\xrightarrow[\text{(gas)}]{}$ $(CH_3)_2C$=CH-CH$_2$Cl + H$_2$O

γ,γ-dimethylallyl chloride (DAC) (60%)

$(CH_3)_2C$=CH-CH$_2$Cl + OHCH$_2$CH=C(CH$_3$)$_2$ $\xrightarrow[\text{1.1 m}]{\text{KOH}}$

1 m   2 m

$O[CH_2CH$=$C(CH_3)_2]_2$ (84%)

Mixed, allylic tertiary vinyl

$(CH_3)_2\overset{|}{\underset{OH}{C}}-CH=CH_2$ + DAC $\xrightarrow[\text{1 mol}]{\text{KOH}}$ $(CH_3)_2C$=CHCH$_2$O$\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH$=CH$_2$

2 mol   1.1 m   (44%)

Dimethylallyl ether

$(CH_3)_2\overset{|}{\underset{ONa}{C}}CH$=CH$_2$ + $(CH_3)_2\overset{|}{\underset{Cl}{C}}CH$=CH$_2$ $\longrightarrow$ crude ether mixture and high boilers (no dimethylallyl ether isolated; cf. Figure 2, G)

3 mol   0.75
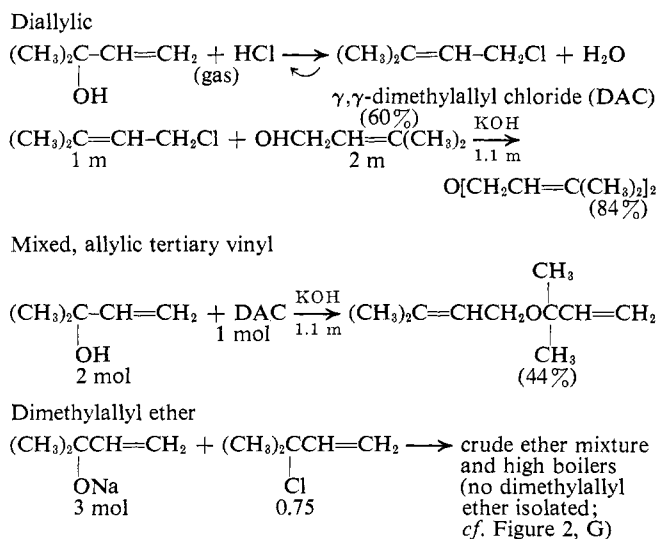
Figure 4. Synthesis of allylic ethers

$$H^+$$
$$(CH_3)_2C=CHCH_2OH \rightleftharpoons (CH_3)_2\overset{+}{C}\cdots CH\cdots CH_2 + H_2O$$
$$(allyl^+)$$

$$(CH_3)_2C=CHCH_2OCH_2CH=C(CH_3)_2$$
$$\text{2 H}_2\text{O} \downarrow \text{2 allyl}^+ \quad (1)$$
$$HOC(CH_3)_2 \quad HOC(CH_3)_2$$
$$(CH_3)_2C=CHCH_2CH-CH_2OCH_2-CHCH_2CH=C(CH_3)_2 + 2H^+$$
$$(3)$$

or

$$HOC(CH_3)_2 \quad HOC(CH_3)_2$$
$$(CH_3)_2C=CHCH_2CH-CH_2-CHCH_2OCH_2CH=C(CH_3)_2$$
$$(4)$$

$$CH_3$$
$$(CH_3)_2C=CH-CH_2-O-C-CH=CH_2$$
$$\text{2 H}_2\text{O} \downarrow \text{2 allyl}^+ \quad CH_3 \quad (2)$$
$$HOC(CH_3)_2 \quad CH_3 \quad CH_2OH$$
$$(CH_3)_2C=CHCH_2CH-CH_2-O-C-CHCH_2CH=C(CH_3)_2$$
$$(5) \quad CH_3$$

or

$$HOC(CH_3)_2 \quad HOC(CH_3)_2 \quad CH_3$$
$$(CH_3)_2C=CHCH_2CH-CH_2-CHCH_2-O-C-CH=CH_2$$
$$(6) \quad CH_3$$
(excluded by nmr)

Structures (3), (4), (5), (6) = $C_{20}H_{38}O_3$, mol wt 326

Figure 5. Proposed route for high boiling byproducts

Nmr confirmed the ir data and showed by proton area ratios that unlike methyl groups at a double bond [$(CH_3)_2$C=C-] and at a saturated carbon [$(CH_3)_2$C<] were equal. This strongly indicated the presence of methyl butenyl and 2-propanol groups. Methylene protons next to oxygen were noted and supported the presence of an ether group ($-CH_2-O-CH_2-$), the adjacent, asymmetric carbons of which contained only one proton (CH<). At least two hydroxyl groups per molecule were also supported by the nmr data.

Alternate routes based on cyclization, Diels–Alder additions with isoprene, cationic polymerization or telomerization of the allylic alcohol, or its self addition by hydroxyl-double bond reaction failed to satisfy the nmr requirements. On the basis of analytical data summarized in Table IV, no ready distinction between structures (3), (4), and (5) is possible, particularly in terms of the nmr proton ratios.

The presence of hydroxyl groups (probably tertiary) was shown by the ready dehydration of both high boiling fractions in toluene using a catalytic amount of sulfuric acid.

Table V. Odor Characteristics of Isomerization Products

Product	bp	mm	Odor
3-Methyl-1-buten-3-ol (a)	98	760	Slightly ethereal, camphoraceous
3-Methyl-2-buten-1-ol (b) (Prenol)	140–142	760	Almond, benzaldehyde note
Diallylic ether of (b) (c)	189–191 93–95	760 25	Fresh, green, sweet, anethole note
Mixed allylic–tertiary ether (d)	170–171 74–76	760 25	Similar to (c)
Cond. products of (b) (e)	122–124 124–126	2 2	Farnesol note, sweet
3-Methyl-1-penten-3-ol (f)			Green, camphoraceous
3-Methyl-2-penten-1-ol (g)	98–100	80	Almond, furfural note
Diallylic ether of (g) (h)	140–142	50	Green, floral, pleasant, slight anethole note
Cond. products of (g) (i)			Farnesol note, sweeter than (e)

Table IV. High Boiling Byproducts (Methyl Butenol)

	C=C Br₂	OH H₂O	Acyl	C	H	O	mol wt
(a) 134–135/2 mm	30.6	2.1	10.0	71.8	11.6	17.1	285
(b) 135–137/2 m	30.8	2.2	11.6	72.0	11.6	17.0	326

Calculated values

	C=C Br₂	OH H₂O	Acyl	C	H	O	mol wt
($C_{20}H_{38}O_3$) Figure 5	29.6	2.0	10.4	73.6	11.7	14.7	326

nmr data

Proton area ratio
($C_{20}H_{38}O_3$), (3), (4), (5), Figure 5

	Exp	Calcd	ppm	
H-C=	2	2	5.13	triplet
CH₂O-<	4	4	3.67	complex multiplet
-C=C(CH₃)₂	12	12	1.63	doublet (unequiv)
>C(CH₃)₂	12	12	1.20	doublet (unequiv)
-CH₂, -CH	4–6	6	1.95	multiplet
-OH	~3	2	4.47	broad singlet
Total protons	37–39	38		

Assuming the same molecular weight (326) for both products, a total of 2.1 (a) and 2.2 (b) mol of water was azeotropically removed from both samples, demonstrating more than two hydroxyl groups in the molecule. Acylation (acetic anhydride) values for free hydroxyl supported the dehydration data. Acid-catalyzed bromination gave values (>30%) which best supported four potential double bonds. Simultaneous dehydration and bromination at the resultant isopropenyl sites could account for a total of four double bonds, possibly favoring structures (3) and (4).

Odor Characteristics. Table V summarizes the odors (Tedeschi et al., 1971) of the principal products of isomerization. The crude isomerization mixture from methyl pentenol, when freed of low boiling diene byproduct, has a pleasant, green, lavender odor. The diallylic and mixed isomeric ethers from different alkenols have almost identical odors. The ethers derived from methyl pentenol are particularly interesting since they possess a fresh, green, floral odor and could be used as main components in perfumes. The

qualitative odor evaluations were carried out by a professional perfumer.

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End of Part I of Symposium on The Chemistry of Essential Oils and Related Products. Other papers will be published in a later issue.