

(8) (a) Burton and Ingold, *J. Chem. Soc.*, 915 (1928); (b) for review see Catchpole, Hughes and Ingold, *ibid.*, 1-17 (1948).

differences in mobility of these various allylic acetates is related to inductive and tautomeric effects of the groups attached to their carbinyl carbon atoms.⁹

TABLE II

REARRANGEMENT OF THE α - AND γ -METHYLALLYL (METHYL-VINYLCARBINYL AND CROTYL) ACETATES IN ACETIC ACID CONTAINING 0.3 MOLE PER LITER OF *p*-TOLUENESULFONIC ACID, AT 60°

Pure methylallyl acetate used	Time, days	Composition of acetates, ^a %		Recovery of purified esters, %
		Secondary	Primary	
Secondary	9	35	65	41
Secondary	16	36	64	30
Primary	16	35	65	31

^a It is interesting to compare this composition with that of the trichloroacetates, which rearrange in acetic anhydride at 140° to a mixture which is 55% secondary and 45% primary methylallyl trichloroacetates. Burton, *J. Chem. Soc.*, 248 (1930).

Experimental Part

α, α -Dimethylpropargyl alcohol and α -ethyl- α -methylpropargyl alcohol were prepared in 71 and 80% yields, respectively, according to Campbell, *et al.*,¹⁰ and purified by fractional distillation. α, α -Dimethylpropargyl alcohol, b.p. 102–102.5°, n_D^{20} 1.4186. N-Phenyl carbamate, needles from isopropyl ether-petroleum ether, m.p. 101–101.5°. *Anal.* Calcd. for $C_{12}H_{12}O_2N$: C, 71.0; H, 6.5. Found: C, 71.0; H, 6.8. α -Ethyl- α -methylpropargyl alcohol, b.p. 120–120.5°, n_D^{20} 1.4286. N-Phenyl carbamate, needles from petroleum ether, m.p. 65–66.5°. *Anal.* Calcd. for $C_{13}H_{14}O_2N$: C, 71.9; H, 7.0. Found: C, 72.2; H, 6.8.

α, α -Dimethylallyl alcohol and α -ethyl- α -methylallyl alcohol were prepared by hydrogenating the propargyl alcohols, without solvent, in a Burgess-Parr low pressure machine with a catalyst of palladium deposited on barium sulfate. After the calculated amount of hydrogen had been absorbed, the catalyst was filtered and the allyl alcohol distilled. A sample of each was fractionated to show that no allylic rearrangement had taken place. α, α -Dimethylallyl alcohol, b.p. 99.7–101°, n_D^{20} 1.4166 (lit.,¹¹ b.p. 96.1–97.1° (744 mm.). n_D^{20} 1.4168). N-Phenyl carbamate, prisms from petroleum ether, m.p. 60–62.5°. *Anal.* Calcd. for $C_{12}H_{14}O_2N$: C, 70.2; H, 7.4. Found: C, 70.3; H, 7.6. Allophanate,¹² prisms from ethanol, m.p. 138.5–140.0°. *Anal.* Calcd. for $C_7H_{12}O_3N_2$: C, 48.8; H, 7.0. Found: C, 48.7; H, 7.1. Ozonolysis of α, α -dimethylallyl alcohol in hexane at –15° with 3–4% ozonized oxygen until a sample of the solution no longer decolorized dilute bromine in carbon tetrachloride, followed by hydrolysis by Hurd's method¹³ and oxidation of the aldehydes with silver oxide and sodium hydroxide, gave formic acid (yield 78%; Dyer constant¹⁴ observed, 22.4%) and α -hydroxyisobutyric acid (yield 10%), m.p. 76.5–78.5°. Dyer constants determined in this Laboratory for formic acid solutions prepared from C.P. formic acid averaged 22.4%. α -Ethyl- α -methylallyl alcohol, b.p. 117–118°, n_D^{20} 1.4288 (lit.,¹⁵ b.p. 114–116°, n_D^{20} 1.4260). N-Phenyl carbamate, needles from petroleum ether, m.p. 45–47° (lit.,¹⁶ m.p. 40–41°). *Anal.* Calcd. for $C_{13}H_{16}O_2N$: C, 71.3; H, 7.8. Found: C, 71.0; H, 8.0. Allophanate, needles from ethanol, m.p. 123–125.5°. Ozonolysis of α -ethyl- α -methylallyl alcohol as previously described gave formic acid (70%) and α -hydroxy- α -methylbutyric acid (2%), m.p. 70–73°.

Linalyl Acetate and Linalol.—Eastman Kodak Co. technical linalyl acetate was fractionated through a 2.5-foot column packed with glass helices.

Linalyl acetate, b.p. 96° (12 mm.), n_D^{20} 1.4480. Saponification equivalent: calculated, 196 g.; found, 194 g. Number of double bonds per molecule (1Br number): calculated, 2; found, 1.96. Hydrolysis with 10% ethanolic alkali gave only linalol, b.p. 84–85° (12 mm.), n_D^{20} 1.4590. Number of double bonds: found, 1.89.

Esterifications and Isomerizations.—An alcohol (0.4–0.6 mole) and acetic anhydride (0.5–0.7 mole) were heated, unless otherwise specified, at 95° in a water-bath or under reflux. Considerable darkening usually took place. To avoid decomposition of the products during analysis, the reaction mixture was distilled at low pressure. The distillate was poured onto ice and neutralized cautiously with saturated sodium hydroxide. The ice-cold mixture (usually 0.5–1 liter) was extracted repeatedly with ether and the combined extracts dried over magnesium sulfate. The ether was distilled through a column below 36°. Analyses of resulting ester mixtures were made with a three-foot modified Podbielniak fractionating column packed with a Chromel-A spiral. Experimental results are summarized in Table I. α, α -Dimethylallyl acetate, b.p. 49° (55 mm.), n_D^{20} 1.4103 (lit.,¹⁷ b.p. 120–122°, n_D^{20} 1.4120). Saponification equivalent: calculated, 128 g.; found, 128 g. Ozonolysis in hexane at –10° gave α -hydroxyisobutyric acid (35%), m.p. 78.5–80°. Hydrogenation over Adams catalyst gave *i*-amyl acetate (60%), b.p. 120°, n_D^{20} 1.3982.

γ, γ -Dimethylallyl acetate, b.p. 74° (55 mm.), n_D^{20} 1.4298 (lit.,¹⁷ b.p. 120–122°, n_D^{20} 1.4120). Saponification equivalent: calculated, 128 g.; found, 128 g. Ozonolysis in dry ethyl acetate at –15°, followed by hydrogenation of the ozonide over palladium-on-barium sulfate, and fractionation of the resulting solution, gave acetone (yield ca. 50%), identified as the 2,4-dinitrophenylhydrazone, m.p. 123–124°; and acetylglucaldehyde, identified as the 2,4-dinitrophenylhydrazone, yellow cubes from acetone, m.p. 152–153°. *Anal.* Calcd. for $C_{10}H_{16}O_4N_4$: C, 42.6; H, 3.6. Found: C, 42.6; H, 3.9. Hydrogenation of γ, γ -dimethylallyl acetate gave isoamyl acetate (25%), b.p. 140°, n_D^{20} 1.3981. Hydrolysis of γ, γ -dimethylallyl acetate with 20% methanolic alkali gave γ, γ -dimethylallyl alcohol (70%), b.p. 141°, n_D^{20} 1.4433 (lit.,¹⁸ b.p. 140°). N-Phenyl carbamate, prisms from petroleum ether, m.p. 63.5–64.5° (lit.,¹⁸ m.p. 65°). *Anal.* Calcd. for $C_{12}H_{14}O_2N$: C, 70.2; H, 7.4. Found: C, 70.3; H, 7.5. Mixed with α, α -dimethylallyl N-phenyl carbamate, m.p. less than 47°. Allophanate, needles from alcohol, m.p. 160°. *Anal.* Calcd. for $C_7H_{12}O_3N_2$: C, 48.8; H, 7.0. Found: C, 49.1; H, 7.2. Ozonolysis of γ, γ -dimethylallyl alcohol in ethyl acetate at –15°, followed by hydrogenation of the ozonide, gave acetone, identified as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. with an authentic sample, 120–123°.

α -Ethyl- α -methylallyl acetate, b.p. 64° (50 mm.), n_D^{20} 1.4208. Saponification equivalent: calculated, 142 g.; found, 140 g. Number of double bonds: found, 0.985, 0.980. Hydrogenation gave methyl-diethylcarbinyl acetate (60%), b.p. 141°, n_D^{20} 1.4056, which by hydrolysis gave methyl-diethylcarbinol, b.p. 120–123°, n_D^{20} 1.4153.

γ -Ethyl- γ -methylallyl acetate, b.p. 89° (50 mm.), n_D^{20} 1.4353. Saponification equivalent: calculated, 142 g.; found, 140 g. Ozonolysis in ethyl acetate at –15°, followed by hydrogenation of the ozonide, gave acetylglucaldehyde, identified as the 2,4-dinitrophenylhydrazone, m.p. 152–153°. Hydrogenation of γ -ethyl- γ -methylallyl acetate gave 3-methylamyl acetate (40%), b.p. 164–165°, n_D^{20} 1.4079. (Saponification equivalent: calculated, 144 g.; found, 145 g.), which upon hydrolysis yielded 3-methylamyl alcohol, b.p. 152°, n_D^{20} 1.4174. Hydrolysis of γ -ethyl- γ -methylallyl acetate with 1% methanolic alkali gave γ -ethyl- γ -methylallyl alcohol (80%), b.p. 157°, n_D^{20} 1.4475 (lit.,¹⁹ b.p. 156–158°, n_D^{20} 1.4470). Allophanate, needles from alcohol, m.p. 151–151.5°. *Anal.* Calcd. for $C_8H_{14}O_3N_2$: C, 51.6; H, 7.6. Found: C, 51.6; H, 7.6. Ozonolysis of γ -ethyl- γ -methylallyl alcohol in hexane at –10° gave ethyl methyl ketone, identified as the 2,4-dinitrophenylhydrazone, m.p. 109–110°.

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- (13) Hurd and Williams, *THIS JOURNAL*, **58**, 2636 (1936).
- (14) Dyer, *J. Biol. Chem.*, **28**, 450 (1917).
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- (17) Nazarov and Azerbaev, *J. Gen. Chem.*, **18**, 407 (1948).
- (18) Courtot, *Bull. soc. chim.*, [3] **35**, 657 (1906).
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Esterifications of Linalol in Acidic Media.—Linalol (40 g., 0.26 mole) and acetic anhydride (30 g., 0.3 mole) were refluxed 10 hours (135°). The reaction mixture was worked up and the product fractionated. The fraction boiling at 55–60° (12 mm.) was assumed to be trienes with the formula $C_{10}H_{16}$ (13.5 g., 40% yield).

Geranyl acetate, b.p. 118° (12 mm.), n_D^{25} 1.4600 (18.5 g., 36% yield). Saponification equivalent: calculated, 196 g.; found, 198 g. Number of double bonds: calculated, 2; found, 1.91. Residue, about 10 ml.

Linalyl acetate (50 g., 0.25 mole), acetic acid (225 ml.) and phosphoric acid (1.5 ml. of 85%) were allowed to stand 66 hours at 25°. The products consisted of a fraction boiling at 56–60° (12 mm.), n_D^{25} 1.4726 (6.5 g.), and geranyl acetate, b.p. 116–121° (12 mm.), n_D^{25} 1.4610 (27 g., 54% yield); residue, 7.3 g.

Isomerization of Primary Allylic Acetates with Strong Acid.— γ , γ -Dimethylallyl acetate (16 g.), acetic anhydride (15 g.) and acetic acid (5 g.) were heated 116 hours at 95°. The primary acetate was recovered to the extent of 90%, b.p. 70.5° (40 mm.). There was some residue but no tertiary acetate.

A solution of geranyl acetate (20 g.), glacial acetic acid (100 ml.) and 85% phosphoric acid (10 ml.) stood 9 days. The light brown solution yielded 1.3 g. with b.p. 57–60° (12 mm.), n_D^{25} 1.4779, and geranyl acetate, b.p. 115–116° (12 mm.), n_D^{25} 1.4610 (10.7 g., 54% recovery); residue, 4.5 g.

Esterification of Linalol in Basic Medium.—Linalol (34 g., 0.22 mole), acetic anhydride (28 g., 0.28 mole) and pyridine (24 g., 0.3 mole) were heated 110 hours at 95°. The black solution was diluted with ether, washed with water, dilute sulfuric acid, dilute alkali and dried over magnesium sulfate. Ether was evaporated and the residue fractionated. Linalyl acetate only was received, b.p. 96° (12 mm.), n_D^{25} 1.4480 (33 g., 75% yield).

α -Ethyl- α -methylallyl acetate was recovered unchanged (85% recovery) after being heated 11 days at 95° with acetic anhydride which had been previously freed of acetic acid by fractional distillation.

Rearrangement of α - and γ -Methylallyl Acetates.—A glacial acetic acid (82 g., reagent grade) solution, 3 moles per liter in crotyl acetate (38.5 g.) and 0.3 mole per liter in *p*-toluenesulfonic acid (6.0 g., crystalline), was heated at 60°. The volatile material, presumably butadiene, was determined by weighing the flask before and after the reaction period; there was no appreciable difference in weight in any experiment. The black reaction mixture was distilled at low pressure and the distillate poured onto ice. The acetic acid was neutralized with alkali, and the solution extracted repeatedly with ether. The ester mixture was analyzed with the three-foot modified Podbielniak fractionating column; results are shown in Table II. The amounts of residual material obtained in these experiments were not sufficient to account for the remainder of the yields. α -Methylallyl acetate, b.p. 112.5°, n_D^{25} 1.4048; γ -methylallyl acetate, b.p. 132–133°, n_D^{25} 1.4183.

Summary

1. The acylations of α , α -dimethylallyl alcohol, α -ethyl- α -methylallyl alcohol and linalol are reported.

2. In acidic media their acetates have been found to rearrange completely into the corresponding primary isomers, γ , γ -dimethylallyl acetate, γ -ethyl- γ -methylallyl acetate and geranyl acetate, respectively.

3. α -Methylallyl acetate and γ -methylallyl acetate have been found to rearrange in acetic acid at 60° under the influence of *p*-toluenesulfonic acid to mixtures of acetates which contain 35% of the secondary isomer and 65% of the primary isomer.

LOS ANGELES 24, CALIF.

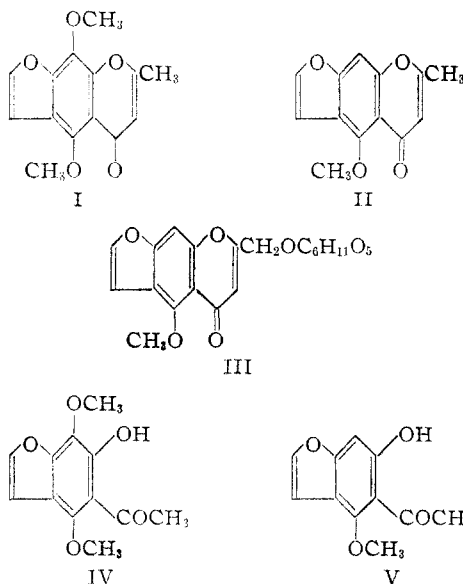
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Chromones. II. The Synthesis of Visnaginone

BY T. A. GEISSMAN AND ELLY HINREINER

The fruit of the umbelliferous plant *Ammi visnaga* contains the structurally related chromones khellin (I), visnagin (II) and khellol glucoside (III).



Upon alkaline degradation, khellin yields khellinone (IV)¹ and both visnagin and khellol glucoside yield visnaginone (V).² The partial,^{1,3} from khellinone, and total^{4,5,6,7} syntheses of khellin have been accomplished by several independent investigators. The total synthesis of visnaginone has recently been reported by Gruber and Horváth⁸ in a preliminary note which became accessible after the completion of the work described in this paper.

While the synthesis of khellinone (from 2,5-dimethoxyresorcinol) involves no problems in the orientation of the furo- and chromone rings, that of visnaginone is not so straightforward so far as questions of orientation are concerned. Indeed, the initial attempts of Gruber and Robertson and their collaborators to prepare it led only to isovisnaginone (VI), from which isovisnagin (VII) was prepared.^{9,10}

- (1) Späth and Gruber, *Ber.*, **71B**, 106 (1938).
- (2) Späth and Gruber, *ibid.*, **74B**, 1492 (1941).
- (3) Geissman, *THIS JOURNAL*, **71**, 1498 (1949).
- (4) Baxter, Ramage and Timson, *J. Chem. Soc.*, S30 (1949).
- (5) Clarke and Robertson, *ibid.*, 302 (1949).
- (6) Murti and Seshadri, *Proc. Indian Acad. Sci.*, **30**, 107 (1949).
- (7) Geissman and Halsall, *THIS JOURNAL*, in preparation.
- (8) Gruber and Horváth, *Monatsh.*, **80**, 874 (1949).
- (9) Clarke, Glaser and Robertson, *J. Chem. Soc.*, 2261 (1948).
- (10) Gruber and Horváth, *Monatsh.*, **80**, 563 (1949).