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

Allylic Rearrangements. XXX. The Formation and Rearrangement of α,α-Dialkylallyl Acetates[1]

BY WILLIAM G. YOUNG AND IRVING D. WEBB

Numerous investigators have studied, or employed as important steps in lengthy syntheses, the allylic rearrangements of α,α-dialkylallyl alcohols (I) into derivatives of the corresponding γ,γ-dialkylallyl alcohols (II).[2] Such an allylic rearrangement is represented by equation (1), in which R and R′ represent alkyl radicals of widely varied constitution, and X represents hydroxyl, acetate, chloride or bromide. In all the publications which came under surveillance by the present authors, it was reported, or assumed, that complete conversion of the tertiary allylic alcohol (I) into its corresponding primary derivative (II) took place when the former was treated with standard

$$\underset{\text{I}}{\mathrm{RR'C(OH)CH{=}CH_2}} = \underset{\text{II}}{\mathrm{RR'C{=}CH{-}CH_2X}}$$

reagents for the reaction.[3] However, experimental data of the investigations referred to indicated that a mixture of tertiary and primary derivatives may frequently be the reaction product. Previous experience in this Laboratory has shown that, when allylic rearrangements occur, mixtures of the two allylic isomers generally result.[4] Accordingly a reinvestigation of the problem of allylic rearrangements of the *gem*-dialkylallyl alcohols and their derivatives was undertaken.

This article reports the results of acylations of α,α-dimethylallyl alcohol, α-ethyl-α-methylallyl alcohol and linalol (III).[5]

$$\mathrm{(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(CH_3)(OH)CH{=}CH_2} \quad \text{III}$$

$$\mathrm{(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CH_2{-}O{-}COCH_3} \quad \text{IV}$$

The esterifications of these three tertiary allylic alcohols with acetic anhydride, at high temperatures for long periods of time, produce as major products the rearranged primary allylic acetates, but none of the tertiary allylic acetates. These results are in substantial agreement with results reported in the literature.

If an esterification is interrupted after a short period of heating, the mixture of products is rich in the tertiary acetate. Such an experiment shows that the tertiary allylic acetate is formed first and subsequently undergoes rearrangement. The rearrangement takes place by influence of acetic acid formed by the esterification reaction, because no rearrangement occurs when a tertiary allylic acetate and pure acetic anhydride are heated together or when a tertiary allylic alcohol is esterified with acetic anhydride in the presence of pyridine. That the rearrangement is catalyzed by acid is further demonstrated by experiments in which phosphoric acid was used as catalyst for the acylation of α-ethyl-α-methylallyl alcohol and as catalyst for the rearrangement of linalyl acetate into geranyl acetate (IV). Experimental results are summarized in Table I.

TABLE I

COMPOSITIONS OF ALLYLIC ACETATES PRODUCED BY ESTERIFICATIONS OF TERTIARY ALLYLIC ALCOHOLS WITH ACETIC ANHYDRIDE

Tertiary alcohol	Reaction Temp., °C.	Reaction Time, hr.	Catalyst	Composition of acetates, % Tertiary	Composition of acetates, % Primary	Yield, %[a]
α,α-Dimethylallyl	95	27		70	30	58
	95	215		0	100	51
α-Ethyl-α-methylallyl	120	9		60	40	49
	95	140		0	100	43
	25	18	0.1 M H_3PO_4	0	100	50
Linalol	135	10		0	100	36
	95	110	Pyridine	100	0	75
(Linalyl acetate)	25	66	0.1 M H_3PO_4 in acetic acid	0	100	54
(Geranyl acetate)	25	225	0.1 M H_3PO_4 in acetic acid	0	100	54

[a] Yield calculated from the weight of both esters produced, after purification, and from the weight of alcohol taken.

The low yields of esters obtained in these reactions involving rearrangements are due largely to side reactions such as the formation of unsaturated hydrocarbons (dienes) and resinous substances, both of which were observed throughout this investigation. These two types of by-products are typical of reactions involving carbonium ion intermediates.

It has been known for a long time that secondary and primary allylic alcohols, and saturated tertiary alcohols, and their esters will cleave the alkyl–oxygen bond under the influence of acids and undergo S_N1 or solvolytic-type reactions.[6a,b,7a,b,c] The tertiary allylic acetates show mobilities (ease of rearrangement in S_N1 or solvolytic-type reactions) comparable to α-phenylallyl acetate, which arranges very readily in acetic acid to γ-phenylallyl acetate.[8a,b] However, α- and γ-methylallyl (methylvinylcarbinyl and crotyl) acetates are unaffected by boiling acetic acid[7] but require strong acids to undergo rearrangement (Table II). The

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[1] Abstracted from the thesis submitted by Irving D. Webb for the degree Master of Arts, 1942; Polychemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.

[2] Simonsen, "The Terpenes," Vol. I, Cambridge University Press, London, 1931, pp. 32, 46; Locquin and Wouseng, *Compt. rend.*, **174**, 1711 (1922); Wouseng, *Ann. chim.*, [10] **1**, 343 (1924); Fischer and Löwenberg, *Ann.*, **475**, 192 (1929); Ruzicka and Fischer, *Helv. Chim. Acta*, **17**, 633 (1934); Gould and Thompson, THIS JOURNAL, **57**, 340 (1935); Dimroth, *Ber.*, **71B**, 1333 (1938); and Miescher and Scholz, *Helv. Chim. Acta*, **22**, 120 (1939).

[3] Acetic acid, acetic anhydride with or without pyridine, phosphorus trichloride and pyridine, hydrogen chloride and hydrogen bromide are typical reagents used.

[4] (a) Roberts, Young and Winstein, THIS JOURNAL, **64**, 2157 (1942); (b) Table II.

[5] Nomenclature from Meyer, *Helv. Chim. Acta*, **18**, 282 (1935).

[6] (a) Cohen and Schneider, THIS JOURNAL, **63**, 3382 (1941); (b) Hammond and Rudesill, *ibid.*, **72**, 2769 (1950).

[7] (a) Ruth Warner Van Horn, M.A. Thesis, University of California at Los Angeles (1940); (b) Lawrence Andrews, M.A. Thesis, University of California at Los Angeles (1941); (c) W. G. MacMillan, Research Report, University of California at Los Angles (1941).

[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 (METHYLVINYLCARBINYL 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 trchloroacetates. 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°, $n^{25}\mathrm{D}$ 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°, $n^{25}\mathrm{D}$ 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°, $n^{20}\mathrm{D}$ 1.4166 (lit.,[11] b.p. 96.1–97.1° (744 mm.) $n^{20}\mathrm{D}$ 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 method[13] and oxidation of the aldehydes with silver oxide and sodium hydroxide, gave formic acid (yield 78%; Dyer constant[14] 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°, $n^{20}\mathrm{D}$ 1.4288 (lit.,[15] b.p. 114–116°, $n^{20}\mathrm{D}$ 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.), $n^{25}\mathrm{D}$ 1.4480. Saponification equivalent: calculated, 196 g.; found, 194 g. Number of double bonds per molecule (IBr number): calculated, 2; found, 1.96. Hydrolysis with 10% ethanolic alkali gave only linalol, b.p. 84–85° (12 mm.), $n^{25}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 1.4103 (lit.,[17] b.p. 120–122°, $n^{20}\mathrm{D}$ 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 *t*-amyl acetate (60%), b.p. 120°, $n^{20}\mathrm{D}$ 1.3982.

γ,γ-Dimethylallyl acetate, b.p. 74° (55 mm.), $n^{20}\mathrm{D}$ 1.4298 (lit.,[17] b.p. 120–122°, $n^{20}\mathrm{D}$ 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 acetylglycolaldehyde, identified as the 2,4-dinitrophenylhydrazone, yellow cubes from acetone, m.p. 152–153°. *Anal.* Calcd. for $C_{10}H_{10}O_6N_4$: 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°, $n^{25}\mathrm{D}$ 1.3981. Hydrolysis of γ,γ-dimethylallyl acetate with 20% methanolic alkali gave **γ,γ-dimethylallyl alcohol** (70%), b.p. 141°, $n^{20}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 1.4208. Saponification equivalent: calculated, 142 g.; found, 140 g. Number of double bonds: found, 0.985, 0.980. Hydrogenation gave methyldiethylcarbinyl acetate (60%), b.p. 141°, $n^{25}\mathrm{D}$ 1.4056, which by hydrolysis gave methyldiethylcarbinol, b.p. 120–123°, $n^{25}\mathrm{D}$ 1.4153.

γ-Ethyl-γ-methylallyl acetate, b.p. 89° (50 mm.), $n^{25}\mathrm{D}$ 1.4353. Saponification equivalent; calculated, 142 g.; found, 140 g. Ozonolysis in ethyl acetate at −15°, followed by hydrogenation of the ozonide, gave acetylglycolaldehyde, 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°, $n^{25}\mathrm{D}$ 1.4079. (Saponification equivalent: calculated, 144 g.; found, 145 g.), which upon hydrolysis yielded 3-methylamyl alcohol, b.p. 152°, $n^{25}\mathrm{D}$ 1.4174. Hydrolysis of γ-ethyl-γ-methylallyl acetate with 1% methanolic alkali gave **γ-ethyl-γ-methylallyl alcohol** (80%), b.p. 157°, $n^{20}\mathrm{D}$ 1.4475 (lit.,[19] b.p. 156–158°, $n^{20}\mathrm{D}$ 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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(9) Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

(10) Campbell, Campbell and Eby, THIS JOURNAL, **60**, 2882 (1938).

(11) Campbell and Eby, *ibid.*, **63**, 2683 (1941).

(12) Behal, *Bull. soc. chim.*, [4] **25**, 475 (1919).

(13) Hurd and Williams, THIS JOURNAL, **58**, 2636 (1936).

(14) Dyer, *J. Biol. Chem.*, **28**, 450 (1917).

(15) Nazarov, Rakcheeva, Raigorodskaya and Azerbaev, *Bull. Acad. Sci.* (*U. S. S. R.*), *Classe Sci. chim.*, 305 (1946) (*C. A.*, **43**, 6970 (1949)).

(16) Zal'manovich, *Zhur. Obshchei Khim.* (*J. Gen. Chem*)., **18**, 2103 (1948) [*C. A.*, **43**, 3777 (1949)].

(17) Nazarov and Azerbaev, *J. Gen. Chem.*, **18**, 407 (1948).

(18) Courtot, *Bull. soc. chim.*, [3] **35**, 657 (1906).

(19) Nazarov, Azerbaev and Rakcheeva, *Bull. Acad. Sci.* (*U. S. S. R.*) *Classe. Sci. Chim.*, 419 (1946) [*C. A.*, **42**, 7730 (1948)].

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.), $n^{25}D$ 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.), $n^{25}D$ 1.4726 (6.5 g.), and geranyl acetate, b.p. 116–121° (12 mm.), $n^{25}D$ 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.), $n^{25}D$ 1.4779, and geranyl acetate, b.p. 115–116° (12 mm.), $n^{25}D$ 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.), $n^{25}D$ 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°, $n^{20}D$ 1.4048; γ-methylallyl acetate, b.p. 132–133°, $n^{20}D$ 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.

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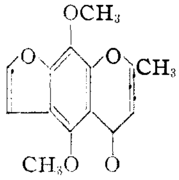
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

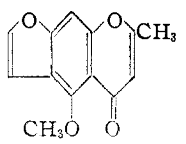
Chromones. II. The Synthesis of Visnaginone

BY T. A. GEISSMAN AND ELLY HINREINER

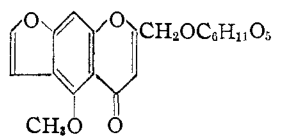
The fruit of the umbelliferous plant *Ammi visnaga* contains the structurally related chromones khellin (I), visnagin (II) and khellol glucoside (III).



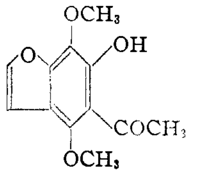
I



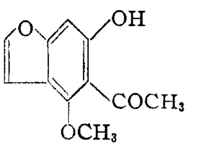
II



III



IV



V

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 Horváth[8] 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]

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[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).