## Study in the Terpene Series. XXXI.[1] Synthesis of Apopinene by Catalytic Decarbonylation of Myrtenal

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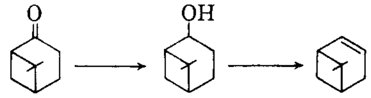
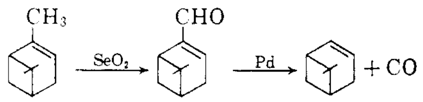
The synthesis of apopinene, 7,7-dimethylbicyclo-[3.1.1.]hept-2-ene, reported in the literature[3] consisted in the hydrogenation of nopinone to nopinol followed by dehydration with potassium acid sulfate:



The nopinone was prepared by a two step process: (a) oxidation of β-pinene with potassium permanganate to nopinic acid and (b) oxidation of the sodium salt of the nopinic acid to nopinone.[4,5] Nopinone was also synthesized in about 40% yield by the ozonolysis of β-pinene.[6–8]

The present paper describes a two-step procedure for the preparation of apopinene from the readily available α-pinene. The first step consists in oxidizing α-pinene to myrtenal and the second step in the catalytic decarbonylation of the aldehyde:



The yield of apopinene produced based on α-pinene used was 55%.

The myrtenal was prepared in 75% yield[8] by oxidizing freshly distilled α-pinene with selenium dioxide, according to the general procedure described by Stallcup and Hawkins.[9] The palladium on barium sulfate catalyst used for the decarbonylation of myrtenal was prepared according to the method described previously.[10]

The myrtenal distilled at 84–85° at 6 mm., $\alpha_D^{20}$ +8°; its 2,4-dinitrophenylhydrazone melted at 222°. The procedure used for the decarbonylation was about the same as described previously.[11] One hundred thirty five grams of the myrtenal and 2.5 g. of freshly prepared 5% palladium hydroxide on barium sulfate were placed in a 1-l. flask provided with a 5 ml. Dean-Stark distillation trap to which was attached a reflux condenser. The top of the latter was connected by means of a rubber tubing to a gas collecting bottle.

Upon heating the catalyst turned black and a strong evolution of carbon monoxide took place. The temperature in the flask dropped after 4 hr. of refluxing from a maximum of 195° to 155°, while the gas evolution dropped from 200 cc. to about 15–20 cc. per min. At this point the distillation trap was opened and 70 g. of apopinene was collected. The remainder in the flask was refluxed for an additional 10 hr. yielding 10 more grams of apopinene and leaving about 15 g. of residue. The total amount of carbon monoxide evolved amounted to 85% of the theoretical.

The apopinene thus obtained was almost pure and distilled at 47–48° at 30 mm., 140.5 at 760 mm., $n_D^{20}$ 1.4678, $d_4^{20}$ 0.8710. The literature[3] reports: b.p. 139.5–140.5, $n_D^{20}$ 1.4670–1.4675, $d_4^{20}$ 0.870.

On hydrogenation the apopinene yielded nopinane (7,7-dimethylbicyclo[3.1.1]heptane) which was identical according to physical constants and infrared spectra with nopinane synthesized previously.[8] The hydrogenation was carried out by dissolving 12.5 g. of the apopinene in 28 ml. of *n*-pentane and hydrogenating it in a 120-ml. capacity rotating autoclave in the presence of 3 g. of nickel—kieselguhr catalyst. The hydrogenation was carried out at 68–80° in the presence of 100 atm. of initial hydrogen pressure. The nopinane distilled at 149°, $n_D^{20}$ 1.4616.

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(1) For paper XXX of this series see H. Pines and C. T. Chen, *J. Am. Chem. Soc.*, **81**, 928 (1959).

(2) Vladimir Ipatieff Postdoctoral Fellow, 1953–55.

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(4) O. Wallach and A. Blumann, *Ann.*, **356**, 227 (1907).

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(6) G. Brus and G. Peyresblaugues, *Compt. rend.*, **187**, 984 (1928).

(7) H. Schmidt, *Z. angew Chem.*, **42**, 126 (1929).

(8) V. N. Ipatieff, G. G. Czajkowski, and H. Pines, *J. Am. Chem. Soc.*, **73**, 4098 (1951).

(9) W. D. Stallcup and J. E. Hawkins, *J. Am. Chem. Soc.*, **63**, 3339 (1941).

(10) H. E. Eschinazi and E. D. Bergmann, *J. Am. Chem. Soc.*, **72**, 5651 (1950).

(11) H. E. Eschinazi, *Bull. soc. chim. France*, 967 (1952).

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## Preparation of 2-Isobutyl-2-methyl-4-trimethylacetoxymethyl-1,3-dioxolane and Its Reaction with Phosphoric Acid

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The addition of aldehydes to poly(vinyl phosphates) was discussed in a recent article.[1] Acetal formation was shown to proceed either by displacement of phosphate by aldehyde or by reaction of aldehyde with the glycol obtained on hydrolysis

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(1) R. A. Barnes, *J. Polym. Sci.*, **27**, 285 (1958).

TABLE I

REACTION OF $H_3PO_4$ AND GLYCIDYL TRIMETHYLACETATE

| Expt. | Acid, % | | Solvent Excess | $H_3PO_4$, Mole % | $H_2RPO_4$,[a] Mole % | $HR_2PO_4$,[a] Mole % |
|---|---|---|---|---|---|---|
| 1 | 100 | $H_3PO_4$[b] | MIBK | 20 | 78 | 2 |
| 2 | 85 | $H_3PO_4$[b] | MIBK | 75 | 25 | 0 |
| 3 | 100 | $H_3PO_4$[b] | $(n\text{-Bu})_2O$ | 49 | 45 | 6 |
| 4 | 85 | $H_3PO_4$[b] | $(N\text{-Bu})_2O$ | 85 | 15 | 0 |
| 5 | 85 | $H_3PO_4$[c] | MIBK | 48 | 52 | 0 |

[a] R = Glyceryl trimethylacetate radical. [b] Equimolar amounts of epoxide and acid stirred at 60°. [c] Ten moles of 86% $H_3PO_4$ were used for one mole of epoxide.

of the phosphate. We have found that ketones will add to "phosphated" polymers such as phosphoric acid treated styrene/glycidyl methacrylate copolymers,[2,3] by an addition similar to that described by Barnes. In order to study the reaction in more detail, a model compound, glycidyl trimethylacetate (GTMA), was prepared and treated with phosphoric acid.

In the presence of excess methyl isobutyl ketone (MIBK) an equimolar mixture of GTMA and 85% phosphoric acid gave a 65% yield of 2-isobutyl-2-methyl-4-trimethylacetoxymethyl-1,3-dioxolane (IMTD). About 25% of the phosphoric acid was converted to a monoalkyl phosphate, and the rest was recovered unchanged. About 10% of the epoxide remained after one hour at 60°. Thus a good yield of ketal, free of tars, was obtained by addition of a ketone to an epoxide whereas earlier workers[4,5] had always obtained large amounts of tar using strong Lewis acid catalysts. A 65% yield of IMTD was also obtained with 5 mole % phosphoric acid rather than an equimolar amount as catalyst.

Although neither our data nor Barnes' defined the actual reaction path for acetal phosphate interchanges, our results indicated that the formation of ketals proceeded most readily under those conditions which favored a glycol intermediate. Under anhydrous conditions, water was not available for glycol formation, and a direct reaction between a ketone and a phosphate ester or an epoxide-phosphate complex was required. With an equivalent of anhydrous orthophosphoric acid 80% of the epoxide was converted to phosphate esters, and less than 20% ketal could have been formed, although in this case the ketal was not isolated (Table I, Expt. 1). By contrast, use of 85% phosphoric acid, which contains approximately an equivalent of water, gave a 65% yield of ketal and only 25% phosphate ester (Expt. 2).

Indirect evidence that the epoxide formed glycols rather than phosphate esters was obtained by heating an equimolar mixture of GTMA and 85% phosphoric acid at 80° under vacuum for five hours. Only 20% of the $H_2O$ present in the phosphoric acid was removed compared to 80% when the acid itself was treated similarly. If phosphoric acid rather than water had added to the epoxide, water would not have been chemically combined with the system and should have been removed.

The preparation of phosphate esters by addition of phosphoric acid to an epoxide was thus best achieved by using anhydrous acids (Expts. 1 *vs.* 2 and 3 *vs.*4). Even an excess of 85% acid was less effective for phosphating an epoxide than an equivalent of 100% acid (Expt. 5 *vs.* 2).

Phosphoric acid was useful for preparing ketals, but the same ketals were also decomposed by the acid, even at room temperature, if excess ketone was not present. On heating at 150° for several hours an equimolar mixture of IMTD and 100% phosphoric acid liberated more than 90% of the MIBK present in the ketal and formed a viscous, brown oil which was soluble in acetone and partly soluble in ether, benzene, and chloroform. The phosphate portion was completely soluble in water and consisted of 30% phosphoric acid, 65% monoalkyl phosphate, and 5% dialkyl phosphate. About 15% of the phosphates in the mixture were present as pyrophosphates.

## EXPERIMENTAL

*Quantitative determination of $H_3PO_4$, $H_2RPO_4$, and $HR_2PO_4$.* The distribution of phosphoric acid between acid and esters was determined by potentiometric titration with $0.1N$ sodium hydroxide. The first break in the titration curve indicated the total amount of strong acid in the system; that is, the first OH in $H_3PO_4$, $H_2RPO_4$, and $HR_2PO_4$. The distance between the first and second breaks indicated the amount of weak acid, that is, the second OH in $H_3PO_4$ and $H_2RPO_4$. The amount of $HR_2PO_4$ was determined by subtracting the amount of weak acid from the strong acid. A second aliquot was titrated after an equivalent of cerous nitrate had been added for each mole of phosphate (determined from the first titration). Cerous ions react with acidic phosphates forming cerous salts and liberate all of the hydrogens as strong acid.[6] The total strong acid in the cerous titration represented $3 \times H_3PO_4$ plus $2 \times H_2RPO_4$ plus $HR_2PO_4$. The amount of $H_3PO_4$ was obtained by subtracting $HR_2PO_4$ plus $2 \times (H_3PO_4$ plus $H_2RPO_4)$ from the total acid in the cerous titration. These two values were obtained from the first titration. The amount of $H_2RPO_4$ was ob-

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(2) M. E. Cupery, U. S. Patent **2,692,876**, (1954).

(3) M. E. Cupery, U. S. Patent **2,723,971**, (1955).

(4) G. Willfang, *Ber.*, **74**, 145 (1941).

(5) M. T. Bogert and B. O. Boblin, Jr., *J. Am. Chem. Soc.*, **55**, 3741 (1933).

(6) E. R. Madsen and T. Kiaersard, *Acta. Chem. Scand.*, **7**, 735 (1953).

tained by subtracting the amount of $HR_2PO_4$ plus $H_3PO_4$ from the strong acid in the first titration.

The amount of pyrophosphate present was determined by Bell's technique using zinc salts.[7]

*Glycidyl trimethylacetate.* GTMA was prepared from trimethylacetic acid and epichlorohydrin according to the technique described in U. S. Patent **2,524,432.** Distilled GTMA was collected between 90.0 and 91.5° at 24 mm. in 81% yield, $n_D^{25} = 1.4219$.

*2-Isobutyl-2-methyl-4-trimethylacetoxymethyl-1,3-dioxolane.* An equimolar mixture of 85% phosphoric acid (79.1 g., 0.70 mole) and GTMA (110 g., 0.70 mole) was stirred for 1 hr. at 60° with a 20-fold mole excess of MIBK (2100 g.). Phosphoric acid and phosphate esters were removed from the reaction mixture by extraction with water in a separatory funnel. The organic layer was dried over anhydrous calcium sulfate and fractionated in a 30 cm. × 6 mm. spinning band column under reduced pressure. IMTD was obtained in 63% yield (112 g.). The product boiled at 120°/7 mm., and had a density of 0.9615 at 25° and an $n_D^{25} = 1.4305$.

*Anal.* Calcd. for $C_{14}H_{26}O_4$: C, 65.08; H, 10.15. Found: C, 65.35, 65.31; H, 10.14, 10.28.

The structure of IMTD was verified by mild acid hydrolysis to glycerol, trimethylacetic acid, and MIBK.

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(7) R. N. Bell, *Anal. Chem.*, **19,** 97 (1947).

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# Reactions of Zirconium Tetrachloride with Acetone

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The metal alkoxides have been studied extensively in recent years for the interesting data which they provide on stereochemical[1] and other fundamental chemical behavior,[2] as well as for their potential industrial applications, as in lacquers[3] and as catalysts.[4] Numerous zirconium alkoxides have been prepared, particularly by Wardlaw, Bradley, and their associates, and their work in this area has been summarized in a recent book.[5]

Acetone in its enol form is an alcohol, and the replacement of its hydroxyl hydrogen by metal should give an alkoxide of the unsaturated alcohol, isopropenol. Only scant attention has been given until the present time to the preparation of zirconium derivatives of acetone or other ketones, and little has been known about them beyond the findings of Jantsch[6] that an addition compound of zirconium tetrachloride and acetone forms at temperatures below about 0°, and that hydrogen chloride is liberated from this addition compound when it is allowed to warm up to somewhat above that temperature.

More recently, we have undertaken a study of the reactions of zirconium tetrachloride with acetone, as a result of the observation by one of us (W. B. B.) of the formation of colored, pungent, and resinous substances when zirconium tetrachloride solution in acetone is allowed to stand for considerable periods of time. The present paper deals with the preparation and isolation of some of the products of reaction of zirconium tetrachloride and acetone.

## EXPERIMENTAL

*Reagents.* The zirconium tetrachloride used was resublimed from the commercial product; it contained the usual two parts hafnium per 100 parts total metal. Since there is no known reaction in which hafnium behaves qualitatively in a different manner from zirconium, the presence of the hafnium was ignored except for the use of the value 92.25 for the effective atomic weight of zirconium, rather than the standard value of 91.22. The sodium metal and the solvent used were the C.P. grades of commerce. The acetone was treated with a small amount of alkaline potassium permanganate solution to destroy alcohols, and subsequently distilled over anhydrous potassium carbonate and again over anhydrous calcium sulfate.

*Zirconium tetrachloride–acetone addition compound.* A dispersion of 11.7 g. (0.05 mole) of zirconium tetrachloride in 200 ml. of carbon tetrachloride was prepared at room temperature and then cooled in an ice and salt bath to −5° and held at this temperature. To the stirred suspension, 25 ml. (0.34 mole) of previously chilled acetone was added dropwise, over an hour's time. The zirconium tetrachloride appeared to dissolve, and a new white precipitate formed immediately. The stirring was continued for 2 hr. after the addition of the acetone, and the slurry was then filtered rapidly and the precipitate was washed with chilled acetone. The filter cake was finally dried under vacuum at −5°, and sealed into glass tubes for storage.

Analysis of the product indicated it to be zirconium tetrachloride monoacetonate.

*Anal.* Calcd. for $ZrCl_4 \cdot CH_3COCH_3$: Zr, 31.6; Cl, 48.5; C, 12.3; H, 2.1%. Found: Zr, 31.8; Cl, 47.8; C, 12.1; H, 1.9%.

*Trichlorozirconium isopropenoxide.* A dispersion of 11.7 g. of zirconium tetrachloride in 200 ml. of carbon tetrachloride was prepared at room temperature, and 100 ml. of acetone was added dropwise. Hydrogen chloride was evolved during the addition and for some time following. The pale yellow solution was filtered, avoiding contact with the atmosphere, to remove traces of insolubles derived from the zirconium tetrachloride. The filtrate was mixed with 100 ml. of benzene and refluxed. Hydrogen chloride continued to be evolved slowly for several hours, and a pale brown solid formed. This was filtered off and washed with acetone, then dried under vacuum.

The observations made during the experiment suggest that initially a carbon tetrachloride- and benzene-soluble trichlorozirconium isopropenoxide, containing acetone of solvation, was formed, but on refluxing acetone was split

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(1) D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 5020 (1952).

(2) D. C. Bradley, F. M. Abd-el-Halim, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 4960 (1952).

(3) I. C. Kraitzer, F. K. McTaggart, and W. Winter, *The Preparation and Utilization of Esters of Ortho Titanic Acid*, Council for Scientific and Industrial Research, Commonwealth of Australia, Serial No. 64. December, 1947.

(4) J. R. Caldwell and J. W. Wellman, U.S. Patent **2,727,881,** Dec. 20, 1955.

(5) Blumenthal, W. B., *The Chemical Behavior of Zirconium*, Van Nostrand, 1958, pp. 352–62.

(6) G. Jantsch, *J. prakt. Chem.*, **115,** 7–8 (1927).