# *The Rearrangement Reaction of Levulinic Acid in a Selenium Dioxide-catalyzed Hydrogen Peroxide Oxidation*

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In previous reports[1-4] we described the synthesis of carboxylic acids from dialkyl ketones and aryl alkyl ketones by oxidation with hydrogen peroxide using a selenium dioxide catalyst. Our findings have shown that the process of the formation of carboxylic acids from an unsymmetrical dialkyl ketone involved the migration of one of the alkyl groups to the $\alpha$-carbon atom of the other

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alkyl group and the oxidation of the carbonyl group to a carboxyl group. This observation led us to guess that keto-acid might be oxidized to dibasic acid with the same number of carbon atoms as the original keto-acid; therefore, levulinic acid was used as the starting material.

The oxidation of levulinic acid with hydrogen peroxide was carried out in a tertiary butyl alcohol solution in the presence of a catalytic amount of selenium dioxide at 82°C. Distillation of the reaction mixture under reduced pressure afforded glutaric acid as the main acid product; a small amount of methylsuccinic acid was also isolated as the isomer of glutaric acid.

Several studies[5-11] have been made of the syntheses of glutaric acid derivatives from levulinic acid. Hara and Fujise[5] have reported the one-step synthesis of glutaramide from levulinic acid by a Willgerodt reaction, and recently Motoki and Odaka[9-11] have studied a method for the syntheses of various derivatives of glutaric acid. In these cases, however, no rearrangement of the carbon skelton was observed, because these reactions proceeded via a process involving the reduction of the carbonyl group and the oxidation of the active methyl group. In the present case, glutaric acid may be formed by the intramolecular migration of the $\beta$-carboxyethyl group to the methyl carbon atom and by the oxidation of the original carbonyl group to the carboxyl group; these possibilities are based on the rearrangement behavior[1,12] of unsymmetrical dialkyl ketones. Furthermore, the evidence of the rearrangement was supported by the fact that the methylsuccinic acid isolated was produced by the migration of the methyl group to the methylene carbon atom adjacent to the carbonyl group:

$$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}COOH \xrightarrow{H_2O_2\text{-}SeO_2}$$

$$HOOC\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$$

$$+\ HOOC\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_2\text{-}COOH$$

It has been shown that the active species of this rearrangement reaction may be peroxyselenous acid $\left(HOO\text{-}Se\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}\right)$ generated by the oxidation of selenium dioxide with hydrogen peroxide in the reaction system,[12] so that the rearrangement may be caused by the attack of peroxyselenous acid on levulinic acid in a process similar to that described in the previous reports.[4,12]

The reactivity of levulinic acid was considerably lower than that of dialkyl ketone with a low molecular weight, so that the yield of $C_5$-dibasic acids amounted to about 10% of the levulinic acid used, and a fairly good recovery of the starting levulinic acid was observed in spite of an excess amount of hydrogen peroxide having been used.

Small amounts of $\beta$-acetylacrylic acid and of fumaric acid were also isolated as by-products. Raymond[13] has reported that the oxidation of various esters of levulinic acid yielded the corresponding esters of $\beta$-acetylacrylic acid by dehydrogenation. Accordingly, it was assumed that $\beta$-acetylacrylic acid might be produced by the action of the selenium dioxide used as the catalyst in the present case:

$$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}COOH \xrightarrow{SeO_2}$$

$$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH{=}CH\text{-}COOH$$

Fumaric acid may be generated by the oxidative cleavage of $\beta$-acetylacrylic acid or by the dehydrogenation of succinic acid[14] with selenium dioxide. Succinic acid can be formed by the oxidative cleavage of levulinic acid, but the formation of succinic acid was not detected in the present experiment.

## Experimental

**Material.**—Levulinic acid used in this experiment was purified by the distillation of the commercial product; b. p. 152°C/21 mmHg (reported[15] b. p. 138~140°C/10 mmHg).

**Oxidation of Levulinic Acid.** — To 150 ml. of a tertiary butyl alcohol solution[16] containing 1.0 g. of selenium dioxide and 0.3 mol. of hydrogen peroxide, 17.4 g. (0.15 mol.) of levulinic acid was added. The hydrogen peroxide was completely consumed by the refluxing of the solution for

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16) For the preparation of the oxidative reagent, see Ref. 1.

12 hr., and at this stage a small amount of metallic selenium was deposited. After the removal of the solvent by distillation from the reaction mixture, the residual high-boiling liquid was distilled under reduced pressure and was divided into two fractions: fraction A, 11.5 g., b. p. <150°C/3.5 mmHg; fraction B, 2.8 g., b. p. 150~160°C/3.5 mmHg; residue, ca. 2.5 g., resinous substance containing metallic selenium.

Fraction A was kept for two days at room temperature, and the deposited crystalline material was then fitered (0.5 g.) and recrystallized from benzene to yield 0.3 g. of β-acetylacrylic acid; m. p. 125°C (reported[17] m. p. 125~126°C). Upon admixture with an authentic sample of β-acetylacrylic acid, the melting point was not depressed, and the infrared spectrum of the product was identical with that of an authentic sample.

Found: C, 52.61; H, 5.48. Calcd. for $C_5H_6O_3$: C, 52.63; H, 5.30%.

After the removal of β-acetylacrylic acid by filtration, the residual liquid was redistilled under reduced pressure, giving a trace amount of β-acetylacrylic acid and 8.7 g. of unchanged levulinic acid; the infrared spectra of these samples closely resembled those of authentic materials.

Fraction B, which partly contained crystalline materials, was cooled at 0°C overnight, and the solid which was then deposited was filtered and dissolved into hot benzene. After the removal of a small amount of insoluble substance, the hot benzene solution was cooled and the crystalline material deposited was filtered and recrystallized from benzene to yield 1.2 g. of glutaric acid; m. p. 96~97°C (lit.[18] m. p. 97°C)). Upon admixture with an authentic sample of glutaric acid, the melting point was not depressed, and the infrared spectrum of the product was identical with that of an authentic sample.

Found: C, 45.67; H, 6.22. Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10%.

The substance insoluble in hot benzene was purified three times by sublimation at 200°C/25 mmHg, yielding 0.03 g. of fumaric acid, which melted at 286~288 °C (sealed tube) (lit..[19] m. p. 286~287°C); the mixed melting point with an authentic sample showed no depression, and the infrared spectrum of the product was identical with that of an authentic sample.

Found: C, 41.67; H, 3.62. Calcd. for $C_4H_4O_4$: C, 41.39; H, 3.47%.

The residual liquid obtained from fraction B by the filtration of the solid materials was cooled at 0°C for a few days, and 0.6 g. of the solid deposited was filtered. After recrystallization was repeated from benzene containing a small amount of ether, there was obtained 0.2 g. of methylsuccinic acid, which melted at 108~109°C (reported[20] m. p. 110°C); the mixed melting point with an authentic sample (m. p. 109~109.5°C), synthesized by the hydrolysis of ethyl β-cyanobutyrate showed no depression, and the infrared spectrum of the product was identical with that of an authentic sample; neutral equivalent, 65.9 (theoretical value, 66.1).

Found: C, 45.13; H, 5.90. Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10%.

## Summary

The selenium dioxide-catalyzed oxidation of levulinic acid with hydrogen peroxide in *t*-butyl alcohol gave glutaric acid and methylsuccinic acid as the rearrangement products. The glutaric acid may be formed by the migration of the β-carboxyethyl group to the methyl carbon atom and by the oxidation of the carbonyl group to the carboxyl group, and the formation of methylsuccinic acid may be due to the migration of the methyl group to the methylene carbon atom adjacent to the carbonyl group.

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