Studies on Lactone Formation in Vapor Phase. III. Mechanism of Lactone Formation from Diols

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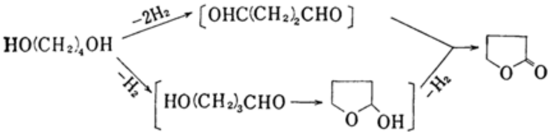
In previous papers[1,2], it was clarified that the catalytic dehydrogenation of 1, 6-hexanediol to ε-caprolactone was very difficult as compared with those of 1, 4-butanediol and 1, 5-pentanediol, and that it yielded 1-cyclopentene-1-carboxaldehyde, cyclopentanecarboxaldehyde and cyclopentylcarbinol as by-products. These facts aroused the author's interest in the mechanism of this reaction. Reppe[3] considered that first dialdehyde or oxyaldehyde was formed and that then an intramolecular reaction of the Cannizzaro type or an intramolecular acetalization, followed by a dehydrogenation to lactone, took place. For example, in the case of 1, 4-butanediol:



Copenhaver[4] wrote that the latter route seemed more likely in view of the nature of the catalyst. Wagner[5] also supported the latter route on the basis of the fact that δ-valerolactone is readily prepared by air oxydation of the corresponding oxyaldehyde[6].

The reactions of dialdehydes or oxyaldehydes leading to the corresponding lactones have, however, been studied by only a few investigators. Meerwein[7] and Longley[8], for instance, prepared δ-valerolactone derivatives by the action of sodium ethoxide or sodium hydroxyde upon dialdehydes in the liquid phase. Bremmer[6] studied the air oxydation of δ-oxyvaleraldehyde to δ-valerolactone in the presence of a cobalt salt in the liquid phase. But the reaction conditions and the catalysts in their investigations are different from those of the dehydrogenation of diols to lactones with the copper catalysts. A study of the behavior of dialdehydes or oxyaldehydes over the copper catalysts used in the previous studies[1,2] has therefore been made.

Experimental

γ-Oxybutyraldehyde (2-oxytetrahydrofuran).—The oxyaldehyde was obtained by thermal decomposition of butane-1, 4-dinitrite in the vapor phase, as has been described by Kuhn[9]. From 50 g. of butanedinitrite (b. p. 62~63°C/23 mmHg, n_D^{25} 1.4049), there was obtained 13 g. of γ-oxybutyraldehyde, b. p. 72°C/18 mmHg, n_D^{25} 1.4400, d_4^{25} 1.0808 (Found: C, 54.47; H, 9.20%). Its infrared spectrum (Fig. 1) showed a strong band due to a hydroxyl group at 2.95 μ and a weak band due to a carbonyl group at 5.80 μ, and it formed a 2, 4-dinitrophenylhydrazone, m. p. 116°C (lit.[9] 120°C).

δ-Oxyvaleraldehyde (2-oxytetrahydropyran). — The oxyaldehyde was prepared by hydrolysis of 3, 4-dihydro-α-pyran[10], as has been described in "Organic Syntheses"[11]. From 60 g. of dihydropyran (b. p. 85~86°C, n_D^{25} 1.4350, d_4^{25} 0.9072), there was obtained 25 g. (33%) of δ-oxyvaleraldehyde, b. p. 54~55°C/3 mmHg, n_D^{25} 1.4515, d_4^{25} 1.0527 (Found: C, 58.63; H, 9.95%). Its infrared spectrum (Fig. 2) showed a strong band due to a hydroxyl group and a weak band due to a carbonyl group, and it formed a 2, 4-dinitrophenylhydrazone, m. p. 106~107°C (lit.[12] 109°C).

1,1,4, 4-Tetraethoxybutane.—1, 1, 4, 4-Tetraethoxy-2-butyne[13] (42 g., b. p. 104°C/3 mmHg, n_D^{25} 1.4319) in 100 ml. of ethanol was hydrogenated under 80 kg./cm² of initial hydrogen pressure with 6 g. of Raney nickel W-6 at 50~60°C for 2 hr. The catalyst was filtered off, and the filtrate was distilled to yield 40.5 g. (92%) of tetraethoxybutane, b.p. 92~93°C/4 mmHg, n_D^{25} 1.4150 d_4^{25} 0.9136 (Found: C, 61.45; H, 11.32%).

Succinaldehyde Dioxime.—A mixture of 47 g. of tetraethoxy butane and 100 ml. of 0.2 N sulfuric acid was stirred at 30°C. After the mixture had been stirred for 2 hr. the water-insoluble layer disappeared. After another 2 hr., 34 g. of hydroxylamine chloride was added. Then, 50 g. of anhydrous sodium carbonate was added in small portions. After the mixture had been kept in the refrigerator overnight, the crystals were filtered, washed with

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1) S. Oka, This Bulletin, **34**, 12 (1961).
2) S. Oka, ibid., **35**, 562 (1962).
3) W. Reppe et al., *Ann.*, **596**, 159 (1955).
4) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry", Reinhold Pub. Co., New York (1949), p. 152.
5) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry", John Wiley & Sons., New York (1953), p. 536.
6) J. G. M. Bremmer et al., U. S. Pat., 2429799 (1947); *Chem. Abstr.*, **42**, 923 (1948).
7) H. Meerwein, *Ber.*, **53**, 1829 (1920).
8) R. I. Longley et al., *J. Am. Chem. Soc.*, **72**, 3079 (1950).
9) L. P. Kuhn et al., ibid., **78**, 2719 (1956).
10) R. L. Sawyer et al., "Organic Syntheses", **23**, 25 (1943).
11) G. F. Woods, ibid., **27**, 43 (1947).
12) G. F. Woods et al., *J. Am. Chem. Soc.*, **68**, 2111 (1946).
13) A. L. Kranzfelder et al., ibid., **60**, 1714 (1938).

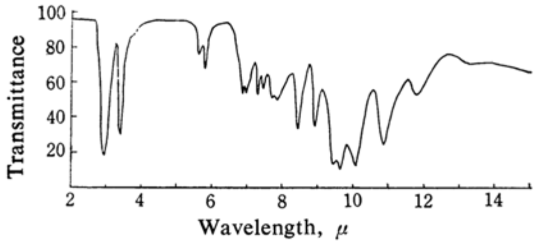

Fig. 1. Infrared spectrum of γ-oxybutyraldehyde.

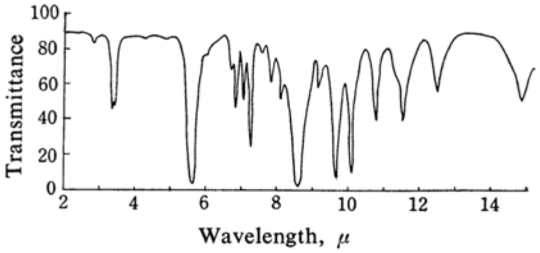

Fig. 4. Infrared spectrum of γ-butyrolactone.

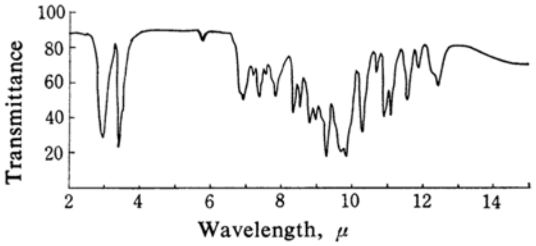

Fig. 2. Infrared spectrum of δ-oxyvaleraldehyde.

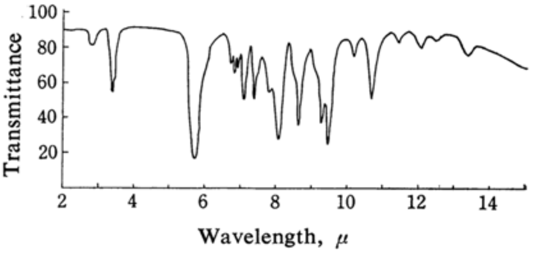

Fig. 5. Infrared spectrum of δ-valerolactone.

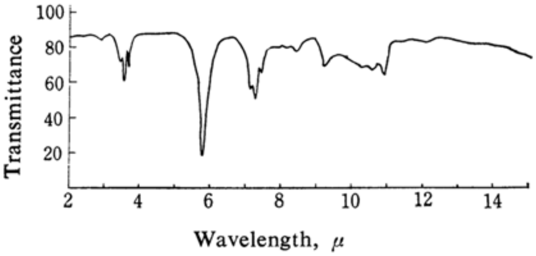

Fig. 3. Infrared spectrum of succinaldehyde.

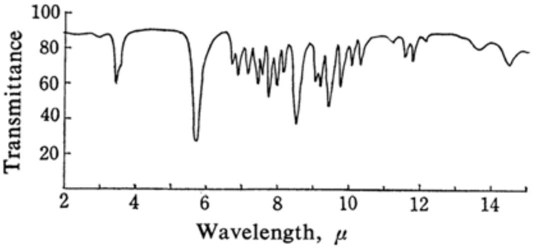

Fig. 6. Infrared spectrum of ε-caprolactone.

water, and dried. The yield of dioxime was 18 g. (74%). Recrystallisation from aqueous ethanol gave a sample melting at 168~169°C (lit.[14] 171~172°C).

Succinaldehyde.—The dialdehyde was obtained by treating its dioxime with sodium nitrite in dilute sulfuric acid, as has been described by Keagle[14]. From 18 g. of the dioxime, there was obtained 6.5 g. (49%) of succinaldehyde, b. p. 78°C/25 mmHg, n_D^{25} 1.4240, d_4^{25} 1.0492 (Found: C, 55.77; H, 7.29%). Its infrared spectrum (Fig. 3) showed a medium band due to C-H group in aldehyde at 3.65 μ and a strong band due to carbonyl group at 5.80 μ.

Glutaraldehyde.—The dialdehyde was prepared by hydrolysis of 2-methoxy-3,4-dihydro-α-pyran, as has been described by Longley[8]. From 30 g. of methoxydihydropyran (b. p. 126~127°C, n_D^{25} 1.4400, d_4^{25} 0.9961), there was obtained 16 g. (61%) of glutaraldehyde, b. p. 53~55°C/3 mmHg, n_D^{25} 1.4280, d_4^{25} 1.0077 (Found: C, 59.14; H, 8.19%). It formed a dioxime, m. p. 164~166°C (Found: C, 46.42; H, 7.83%).

1, 1, 6, 6-Tetraethoxyhexane.— Tetraethoxyhexane was prepared by essentially the same method as that of Kranzfelder[13]. From 150 g. of ethyl orthoformate, 24 g. of magnesium, and 108 g. of tetramethylene bromide, there was obtained 62 g. (47%) of tetraethoxyhexane, b. p. 115~117°C/4 mmHg, n_D^{25} 1.4220, d_4^{25} 0.9085. (Found: C, 64.21; H, 11.40%).

Adipaldehyde.—A mixture of tetraethoxyhexane (52 g.) and 0.4 N sulfuric acid (100 ml.) was stirred at 30°C. After the mixture had been stirred for 3 hr., the water-insoluble layer disappeared. The solution was kept at room temperature for another 4 hr. Then the solution was neutralized with sodium bicarbonate, saturated with sodium chloride and extracted with ether. The dried ether extract gave 14 g. (62%) of adipaldehyde, b. p. 110~112°C/20 mmHg, n_D^{25} 1.4335, d_4^{25} 0.9754 (Found: C, 63.13; H, 9.17%). It formed a dioxime, m. p. 170~171°C (Found: C, 49.96; H, 8.58%).

Vapor Phase Reactions. — The apparatus, procedures, and methods for the preparation of the catalysts were essentially the same as those previously described[1,2]. Tablets of the catalyst (50 ml.) were used. The pressure in the reaction system was reduced to 20~30 mmHg. A sample was passed in by vacuum distillation in a period of one hour. The reaction temperature was maintained at 220~230°C. Some experiments are shown below.

γ-Butyrolactone.—The copper-zinc oxide catalyst was used. γ-Oxybutyraldehyde (15 g.) gave a product (13 g.), b. p. 98~100°C/25 mmHg, n_D^{25} 1.4350, which was identified as γ-butyrolactone. It formed a hydrazide, m. p. 92°C, which gave no depression when mixed with an authentic sample.

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[14] L. C. Keagle et al., ibid., 68, 1609 (1946).

δ-Valerolactone.—The copper chromite-zinc oxide catalyst was used. δ-Oxyvaleraldehyde (10 g.) gave a product (6.2 g.), b. p. 73∼74°C/4 mmHg, n_D^{25} 1.4550, which was identified as δ-valerolactone. It formed a hydrazide, m. p. 105∼106°C, which gave no depression when mixed with an authentic sample.

The infrared spectra of the lactones obtained in the present work (Figs. 4—6) showed strong bands due to lactone group at 5.75 and 8.60 μ.

1-Cyclopentene-1-carboxaldehyde. — The copper chromite-zinc oxide catalyst was used. Adipaldehyde (10 g.) gave a product (4.5 g.), b. p. 55∼57°C/25 mmHg, n_D^{24} 1.4765, d_4^{25} 0.9522, which was identified as 1-cyclopentene-1-carboxaldehyde (lit.[15] b. p. 57∼59°C/27 mmHg, n_D^{20} 1.4866). MR_D Found: 27.1. Calcd.: 27.3.

Found: C, 74.62; H, 8.79. Calcd. for C_6H_8O; C, 74.97; H, 8.39%.

Cyclopentenecarboxaldehyde gave a 2,4-dinitrophenylhydrazone melting at 209∼210°C (lit.[16] 210∼211°C).

Found: C, 52.16; H, 4.48. Calcd. for $C_{12}H_{12}O_4N_4$: C, 52.17; H, 4.38%.

Cyclopentylcarbinol. — The copper-magnesium oxide catalyst was used. Unlike as in the above experiment, adipaldehyde (10 g.) was passed in with a steady current of hydrogen (20 l./hr.) in a period of one hour. The reaction temperature was maintained at 230∼240°C. The product (5.2 g.), b. p. 75∼78°C/25 mmHg, n_D^{25} 1.4550, d_4^{25} 0.9309, was identified as cyclopentylcarbinol. It formed a phenylurethan, m. p. 108°C, which gave no depression when mixed with an authentic sample.

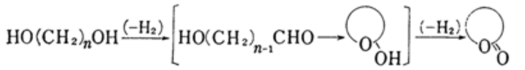
Results and Discussion

The results are summarized in Table I. With all the catalysts used, it was ascertained that the oxyaldehydes gave the corresponding lactones as easily as the diols did. On the contrary, the dialdehydes examined gave no lactones, and they were recovered up to 70% except in the case of adipaldehyde. Adipaldehyde gave 1-cyclopentene-1-carboxaldehyde even in the presence of the copper chromite-zinc oxide catalyst which was the most favorable catalyst for ε-caprolactone formation. Adipaldehyde gave cyclopentylcarbinol as well as 1,6-hexanediol, under a hydrogen stream over the copper-magnesium catalyst. From these experimental results, it is concluded that the dehydrogenation of the diols to the lactones proceeds according to the latter route mentioned above, although the formation of ε-caprolactone from ε-oxycaproaldehyde could not be examined.

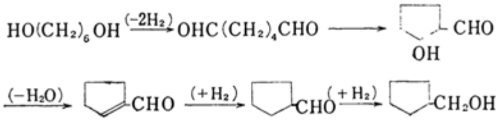
TABLE I. LACTONE FORMATION FROM DIOLS, OXYALDEHYDES AND DIALDEHYDES

Catalyst	Copper-zinc oxide	Copper chromite	Copper chromite-zinc oxide
Sample	Yield of lactone %	Yield of lactone %	Yield of lactone %
1,4-Butanediol	95	53	78
γ-Oxybutyraldehyde	93	53	80
Succinaldehyde	0	0	0
1,5-Pentanediol	84	54	76
δ-Oxyvaleraldehyde	76	55	65
Glutaraldehyde	0	0	0
1,6-Hexanediol	trace	28	68
Adipaldehyde	0	0	0

Reaction temperature: 220∼230°C. Reaction time: 1 hr.



The products obtained from adipaldehyde support the occurrence of the side reaction proposed in the previous paper[2].



From a study of the ultraviolet spectra, Hurd et al.[17] concluded that, in aqueous dioxane, γ-oxybutyraldehyde and δ-oxyvaleraldehyde exist predominantly as cyclic lactoles, and that ε-oxycaproaldehyde exists as 85% free aldehyde. The infrared spectra of γ-oxybutyraldehyde and δ-oxyvaleraldehyde in the present work were in accord with the above results.

The difficulty of lactone formation from 1,6-hexanediol can be understood by considering that of seven-membered lactole ring formation from ε-oxycaproaldehyde. The slow lactole formation would cause undesirable dehydrogenation to adipaldehyde, from which 1-cyclopentene-1-carboxaldehyde is formed by intramolecular aldol condensation followed by dehydration. The occurrence of this side reaction was observed especially in the case of the copper-magnesium oxide catalyst. The high selectivity of the copper chromite-zinc oxide catalyst may be attributed to its accelerating effect on the lactole formation.

Ester formation[18,19] in the dehydrogenation of alcohol to aldehyde with coeppr chromite has been believed to be a result of the Tischtschenko reaction:

$$2RCHO \longrightarrow RCOOCH_2R$$

However, the mechanism of lactone formation

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[15] J. English et al., ibid., **71**, 3310 (1949).

[16] M. S. Klarash et al., *J. Org. Chem.*, **16**, 150 (1951).

[17] C. D. Hurd et al., *J. Am. Chem. Soc.*, **74**, 5324 (1952).

[18] H. Adkins et al., ibid., **55**, 2714 (1933).

[19] R. E. Dunbar, *J. Org. Chem.*, **3**, 242 (1938).

in the present work explains the ester formation more reasonably in the following manner:

$$RCH_2OH \xrightarrow{(-H_2)} RCHO \xrightarrow{(+RCH_2OH)}$$

$$RCH(OH)(OCH_2R) \xrightarrow{(-H_2)} RCOOCH_2R$$

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