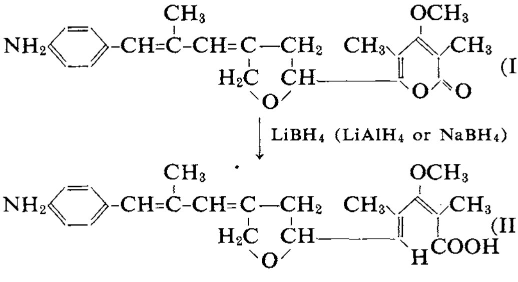
Reduction of α-Pyrones with Complex Metal Hydrides

By Kiyoyuki YAMADA, Mitsuo ISHIZAKA
and Yoshimasa HIRATA

(Received November 21, 1961)

During the course of the structural investigation of aureothin[1], we obtained several derivatives that were regarded as products of unusual reactions. One of the remarkable examples is "aminol H" (II) which was produced from isoaureothamine (I) by treatment with various complex metal hydrides[2].



(I)
(II)

In order to examine whether or not the occurrence of this rather unexpected reduction is due to the complexity of the other part of the molecule, reduction of simple α-pyrones with complex metal hydrides was carried out.

4, 6-Dimethyl-α-pyrone, when treated with lithium aluminum hydride in tetrahydrofuran, gave β-methylsorbic acid, m. p. 97°C[3] (Found: C, 67.00; H, 8.10. Calcd. for $C_7H_{10}O_2$: C, 66.46; H, 7.99%. Ultraviolet spectrum, $\lambda_{\max}^{\mathrm{EtOH}}$, 260 mμ, log ε, 4.0). Reduction of 4, 6-dimethyl-α-pyrone with lithium borohydride in a similar condition also gave the same acid, whereas no reaction took place with sodium borohydride.

Further, lithium aluminum hydride reduction of 4-methoxy-6-methyl-α-pyrone, which is a good model compound for isoaureothamine (I), yielded β-methoxysorbic acid (III) (m. p. 147～149°C (decomp.)[4]. Found: C, 59.17; H, 7.13. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09%. Ultraviolet spectrum, $\lambda_{\max}^{\mathrm{EtOH}}$, 264 mμ, log ε, 4.1) and a neutral product (b. p. 101～104°C/16 mmHg. One methoxyl group. Ultraviolet spectrum; $\lambda_{\max}^{\mathrm{EtOH}}$, 239 mμ) which was shown to be identical with 3-methoxy-2, 4-hexadienol (IV) obtained from β-methoxysorbic acid by lithium aluminum hydride reduction.

The relative amounts of the two products, III and IV, are considerably dependent on the reaction conditions (temperature, manner of addition, etc.), the details of which will be reported elsewhere. Thus, it was established that generally the hydrogenolysis of the 1, 6-linkage of the α-pyrone ring occurs in the reduction using complex metal hydrides.

Chemical Institute
Faculty of Science
Nagoya University
Chikusa-ku, Nagoya

---

[1] K. Yamada, H. Nakata and Y. Hirata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 340 (1960).

[2] K. Yamada, T. Naito, K. Okuhara, H. Nakata and Y. Hirata, This Bulletin, 33, 1303 (1960).

[3] H. Burton and C. K. Ingold, *J. Chem. Soc.*, **1929**, 2022; R. Kuhn and M. Hoffer, *Ber.*, **65**, 651 (1932).

[4] E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, **1949**, 1423; H. B. Henbest and E. R. H. Jones, ibid., **1950**, 3628.