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FORMATION OF α-CHLOROBUTYROLACTONE FROM THE CORRESPONDING α-TRICHLOROACETATE

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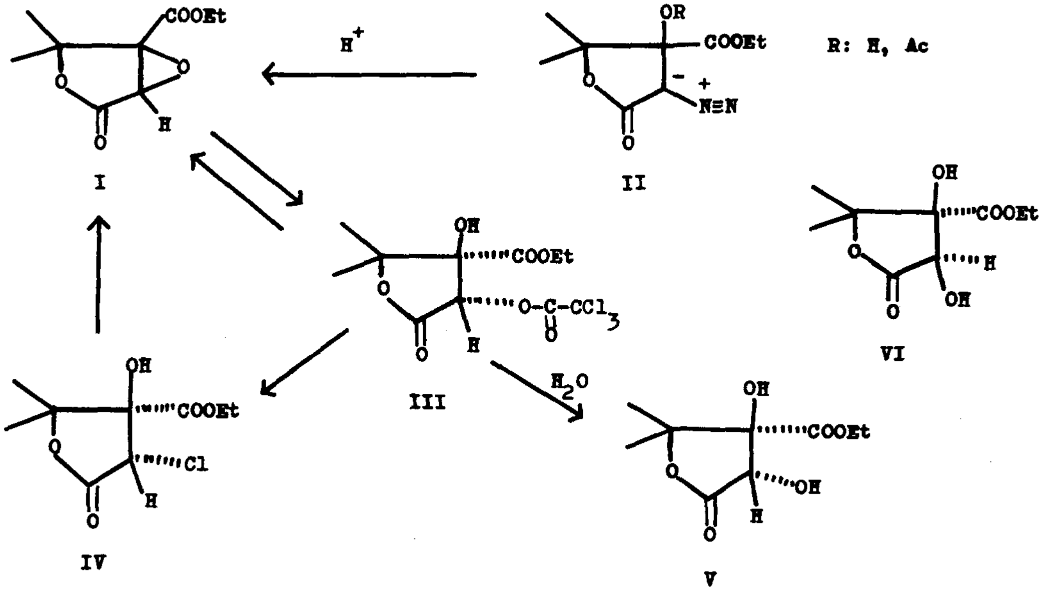
We have recently reported a novel synthesis of α,β-epoxybutyrolactone (I) from α-diazolactone derivatives (II), which can be obtained by nitrosation of the appropriate α-carboxybutyrolactone.[1)] We now wish to describe a ring opening reaction of the epoxylactone (I) by trichloroacetic acid to give the trichloroacetate (III) of the corresponding diol (V). The ester (III) undergoes an inter-



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conversion reaction by treating with saturated sodium bicarbonate solution to afford I and furnishes a mixture of α-chlorolactone (IV) and trans diol (V) together with I on hydrolysis with a highly diluted aqueous solution of sodium bicarbonate, whereas on hydrolysis with water it gives only V. The α-chlorolactone (IV) could also be converted into I, quantitatively, by treating with saturated sodium bicarbonate solution.

The epoxylactone (I) was treated with excess trichloroacetic acid at 120-130° for 5 hours. The product III, purified by crystallization from n-hexane, was obtained in a yield of 78%, m.p. 104.5-105.8°, IR (nujol) 3440 (OH) and 1790 and 1760 (lactone and ester carbonyls) cm^{-1}; NMR ($CDCl_3$) τ 4.03 (1H, singlet, CH_α), 5.5 (2H, quartet, $O-CH_2-C$), 5.80 (1H, singlet, OH), 8.35 and 8.56 (6H, each singlet, gem-dimethyls), and 8.60 (3H, triplet, $O-C-CH_3$). Anal. Calcd. for $C_{11}H_{13}O_7Cl_3$: C, 36.34; H, 3.60. Found: C, 36.47; H, 3.61.

The compound III was treated with aqueous sodium bicarbonate (0.001 mole) for 5 min. The mixture was acidified with dilute sulfuric acid to pH 6.5-7.0 and extracted with ether. The residue which solidified upon removing the fraction of I, 110-120°/2.5 mm, was crystallized from n-hexane-benzene to give V (38.5% yield), m.p. 98.5-99.5°, IR (nujol) 3480 and 3420 (2OH), and 1768 and 1733 (lactone and ester carbonyls) cm^{-1}; NMR (CD_3SOCD_3) τ 3.87 (2H, broad, OH), 4.96 (1H, singlet, CH_3), 5.81 (2H, quartet, $O-CH_2-C$), 8.62 and 8.72 (6H, each singlet, gem-dimethyls), and 8.75 (3H, triplet, $O-C-CH_3$). Anal. Calcd. for $C_9H_{14}O_6$: C, 49.50; H, 6.47. Found: C, 49.51; H, 6.45.

The α-chlorolactone (IV) was obtained in a yield of 18% by extracting with ether from the concentrated aqueous layer of the above experiment. The infrared spectrum of IV showed strong absorption bands at 3440 (OH), 1780 and 1740 (lactone and ester carbonyls) cm^{-1}. The NMR spectrum ($CDCl_3$) had signals at τ 5.17 (1H, singlet, CH_3), 5.60 (2H, quartet, $O-CH_2-C$), 5.85 (1H, singlet, OH), 8.45 and 8.57 (6H, each singlet, gem-dimethyls), and 8.63 (3H, triplet, $O-C-CH_3$). Anal. Calcd. for $C_9H_{13}O_5Cl$: C, 45.68; H, 5.54. Found: C, 45.76; H, 5.62. The Beilstein test gave positive result. It melted at 108.5°.

The establishment of the structure of the trans diol (V) was carried out by comparison with cis diol (VI), m.p. 88.5-89.5°, which was prepared by the stereospecific oxidation$^{2)}$ of ethyl γ,γ-dimethylaconate$^{3)}$ with potassium permanganate. The infrared spectrum of VI (nujol) had strong absorption bands at 3460 and 3250 (2OH), 1765 and 1730 (lactone and ester carbonyls) cm^{-1}. The NMR spectrum ($CDCl_3$) had signals at τ 5.27 (1H, singlet, CH_α), 5.75 (2H, quartet, $O-CH_2-C$), 5.80 (2H, singlet, OH), 8.53 and 8.67 (6H, each singlet, gem-dimethyls), and 8.71 (3H, triplet, $O-C-CH_3$), Anal. Calcd. for $C_9H_{14}O_6$: C, 49.50; H, 6.47. Found: C, 49.67; H, 6.32.

Considering the hydrolysis of the trichloroacetate (III) to give trans diol (V), it should have a trans configuration of hydroxy and trichloroacetoxy groups. 4) The facile conversion of the α-chlorolactone (IV) into the epoxide (I) by treating with dilute sodium bicarbonate solution suggests that the chlorine atom and the hydroxy group of IV may have a trans configuration, hence the conversion of III to V may proceed with the retention of the configuration. Further study is being carried out on the stereospecific reaction of the lactone derivatives (III and IV).

REFERENCES AND FOOTNOTES

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(3) Ethyl γ,γ-dimethylaconate, prepared by esterification of γ,γ-dimethylaconic acid [R. Fittig and B. Frost, *Ann.* 226, 370 (1884)], boiled at 76°/2 mmHg, Anal. Calcd. for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.31; H, 6.78.

(4) The S_N2 type fission of epoxy compounds with trichloroacetic acid has been reported: A. Fürst and R. Scotoni, *Helv. Chim. Acta* **36**, 1410 (1953); J. Elks, G. H. Phillipps, T. Walker, and L. J. Wyman, *J. Chem. Soc.* **1956**, 4330.