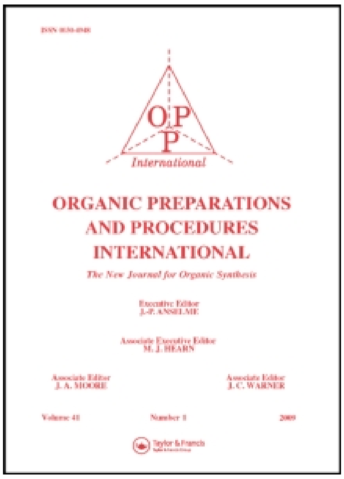

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THE CYCLIC OXALATE ESTERS OF *CIS*- AND *TRANS*-1.2-CYCLOHEXANEDIOLS

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THE CYCLIC OXALATE ESTERS OF cis- AND trans-1,2-CYCLOHEXANEDIOLS

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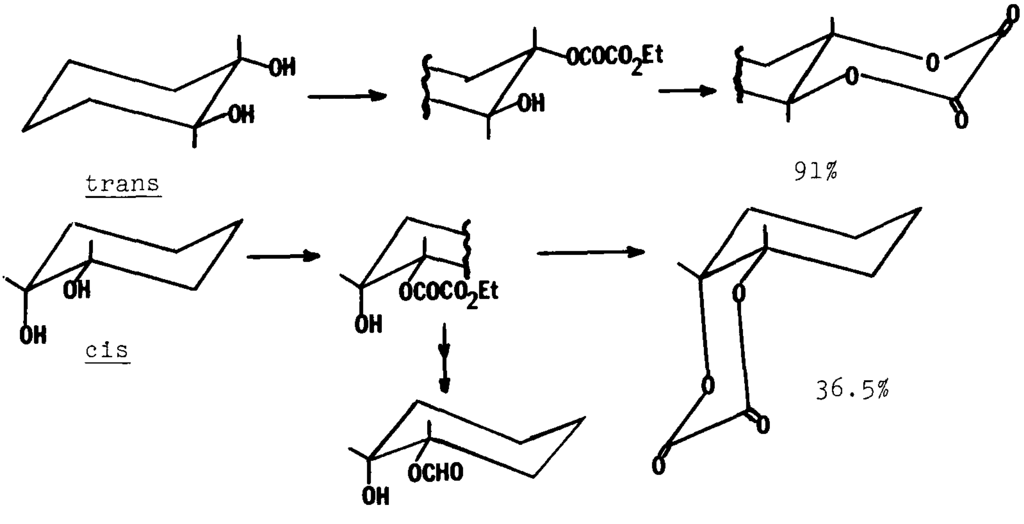
The preparation of the oxalate ester of trans-1,2-cyclohexanediol by the azeotropic distillation of water from a mixture of the diol and oxalic acid proceeded smoothly giving a 91% crude yield of distilled ester. When the same procedure was performed on cis-1,2-cyclohexanediol, however, the crude yield of cyclic ester dropped to 36.5%; the major product was



shown to be the monoformate ester of cis-1,2-cyclohexanediol, by comparison of its nmr and ir spectra and its glc retention time with those of an authentic sample. This is readily explainable by the behavior of the half esters which are presumed to be intermediates in the formation of the cyclic oxalate esters. Chattaway[1] has shown that the monoesters of oxalic acid decarboxylate readily to give formate esters, while the diesters do not. It has been shown that equatorial hydroxyl groups are more readily esterified than axial hydroxyl groups.[2] In the trans isomer both hydroxyl groups are equatorial and the monoester, once formed, will rapidly cyclize. The cis isomer has only one hydroxyl group equatorial and this will preferentially react to form a monoester. The reduced reactivity of the remaining hydroxyl group allows the monoester a longer time to hydrolyze and decarboxylate.

EXPERIMENTAL

Oxalate Ester of trans-1,2-Cyclohexanediol. - The water of hydration, 3.5 ml was removed from 12.6 g (0.1 mole) of oxalid acid dihydrate by azeotropic distillation. Then 11.6 g (0.1 mole) of trans-1,2-cyclohexanediol (Aldrich Co.) was added and the azeotropic distillation was continued until water no longer separated. A total of 3.3 ml of water was collected. The benzene was evaporated and the residue was distilled, affording 15.5 g (91%) of the oxalate ester of trans-1,2-cyclohexanediol, bp. 156-159°/0.5 mm, which crystallized upon cooling, mp. 102-107°. Recrystallization from toluene gave 12.2 g (72%) of the oxalate ester of trans-1,2-cyclohexanediol, mp. 111-112°.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.47; H, 5.92.
Found: C, 56.65; H, 6.05.

ir ($CHCl_3$): ν = 1780 (C=O) cm^{-1}; nmr ($CDCl_3$): δ = 1.50 (complex, 8H), 4.4 (complex, 2H).

Esterification of cis-1,2-Cyclohexanediol with Oxalic Acid. - The water of hydration, 3.5 ml was removed from 12.6 g (0.1 mole) of oxalic acid dihydrate by azeotropic distillation. Then 11.6 g (0.1 mole) of cis-1,2-cyclohexanediol[3] was added and the azeotropic distillation was continued until water no longer separated. The reaction gave 2.7 g (85%) of water. The benzene was removed and the residue was distilled, affording 7.5 g of a clear liquid, bp. 100-120°/1 mm and 6.2 g (36.5%) of a material, bp. 158-159°/0.8 mm which solidified on cooling, mp. 76-81°.

Monoformate and Diformate of cis-1,2-Cyclohexanediol. - The low boiling fraction on redistillation gave 6.5 g of a mixture of the mono- and diformate of cis-1,2-cyclohexanediol, bp. 103-105°/0.8 mm.

ir (CCl_4): ν = 1720 (C=O) cm^{-1}; nmr (CCl_4): δ = 1.5 (complex, 8H) 3.8 (complex, 2H), 8.03 (s, 1/8H), 8.10 (s, 1H).

Cyclic Oxalate Ester of cis-1,2-Cyclohexanediol. - The high boiling fraction was recrystallized from CCl_4 to give 4.3 g (25%) of the cyclic oxalate ester of cis-1,2-cyclohexanediol, mp. 84-84.5°.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.47; H, 5.92.
Found: C, 56.44; H, 6.91.

ir ($CHCl_3$): ν = 1780 (C=O) cm^{-1}; nmr ($CDCl_3$): δ = 1.50

(complex, 8H), 4.4 (complex, 2H).

Esterification of *cis*-1,2-Cyclohexanediol with Formic Acid. - Formic acid 0.46 g (0.01 mole) was added to *cis*-1,2-cyclohexanediol, 1.4 g (0.01 mole) with stirring. After one-half hour at room temperature, the mixture was distilled to give 1.19 g (65%) of the mixed formate esters of *cis*-1,2-cyclohexanediol, bp. 102-4°/0.8 mm.

ir (CCl_4): ν = 1720 (C=O) cm^{-1}; nmr (CCl_4): δ = 1.5 (complex, 8H), 3.8 (complex, 2H), 8.03 (s, 1/4H), 8.10 (s, 1H).

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