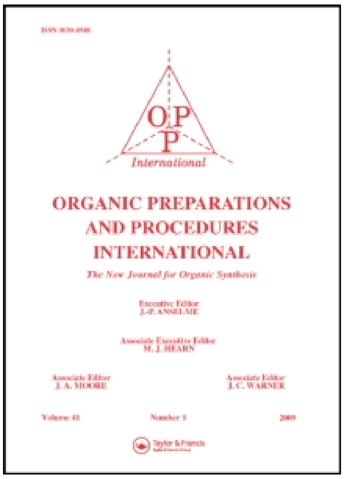


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

LEAD TETRAACETATE OXIDATION OF *CIS*- OR *TRANS*-TETRAHYDROFURAN-2,5-DICARBOXYLIC ACIDS

J. A. Moore[a]; E. M. Partain III[a]
[a] Department of Chemistry, Rensselaer Polytechnic Institute Troy, New York

To cite this Article Moore, J. A. and Partain III, E. M.(1980) 'LEAD TETRAACETATE OXIDATION OF *CIS*- OR *TRANS*-TETRAHYDROFURAN-2,5-DICARBOXYLIC ACIDS', Organic Preparations and Procedures International, 12: 5, 305 — 308

To link to this Article: DOI: 10.1080/00304948009356483

URL: http://dx.doi.org/10.1080/00304948009356483

ORGANIC PREPARATIONS AND PROCEDURES INT. 12(5), 305-308 (1980)

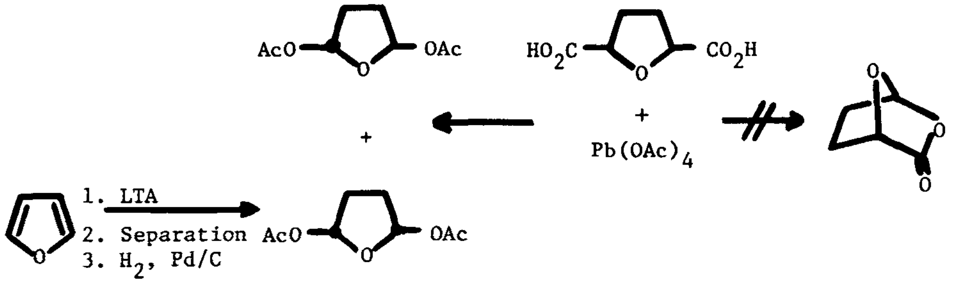
LEAD TETRAACETATE OXIDATION OF *CIS*- OR *TRANS*-TETRAHYDROFURAN-2,5-DICARBOXYLIC ACIDS

J. A. Moore* and E. M. Partain, III[†]

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12181

Dedicated to Professor C.G. Overberger on the Occasion of his 60th Birthday

It has been shown that lead tetraacetate (LTA) oxidation of carbocyclic dicarboxylic acids can be useful in the preparation of lactones.[1] As part of our continuing effort to prepare monomers containing tetrahydrofuran rings,[2] we attempted to apply this approach to the synthesis of 2,7-dioxabicyclo[2.2.1]heptane-3-one.



Under the conditions described below, either *cis*- or *trans*-tetrahydrofuran-2,5-dicarboxylic acid[3] gave a yellow oil boiling at 70°/0.02 torr in about 65% yield. High pressure liquid chromatography (HPLC) showed the product from either isomer to consist essentially of two compounds. Nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy indicated the product to be 2,5-diacetoxytetrahydrofuran, rather than the desired lactone. The assignment of structures to the products was secured by chromatographic comparisons with authentic material prepared by the method of Elming and Clauson-Kaas.[4] It was necessary to make the assignment of structure indirectly *via* the dihydrofuran isomer because the NMR (at 60 mHz) and IR spectra of the tetrahydrofuran isomers are indistinguishable. Pure *cis*-2,5-diacetoxy-2,5-dihydrofuranwas obtained by LTA oxidation of furan, fractional crystallization and catalytic reduction. HPLC of pure *cis*-2,5-diacetoxytetrahydrofuran demonstrated that the product from the LTA oxidation of the tetrahydrofuran dicarboxylic acids with the larger retention volume was the *cis* isomer. The product mixture from the oxidation of the saturated diacid was thus shown to consist of approximately 1/3 *cis*- and 2/3 *trans*-diacetates. This result is in contrast with a distribution of 2/3 *cis*- and 1/3 *trans*-diacetates reported in the literature[4-6] and verified in this work for the product obtained by LTA oxidation of furan followed by catalytic reduction of the mixture of isomers. Previous work indicates that catalytic reduction does not change the isomer distribution.[3,7]

It should be noted that although such intramolecular lactonizations have wide applicability in carbocyclic systems, generalization of this approach to the oxabicyclic system described here does not appear to be promising. If it is desired to obtain either isomer in pure form, this route yields a mixture rich in the *trans* isomer. Separation of mixtures rich in the *cis* isomer, prepared by LTA oxidation of furan, is best achieved by low temperature crystallization[4] followed by column chromatography of the mother liquor, on a mixture of silica gel and cadmium carbonate.[6] The data indicate that preparative separations of the isomers should also be possible using HPLC.

The variable product distribution from the two routes presumably reflects differences in the transition states leading to products from the more flexible saturated diacids or the rigid aromatic furan. The fact that either saturated diacid gives the same product distribution, indicates that the oxidation in these two cases proceeds in a stepwise fashion to give a common intermediate. The complex nature of LTA oxidation[8] prevents more definite mechanistic conclusions being drawn at this time.

EXPERIMENTAL

NMR spectra were recorded on a Varian model T-60A spectrometer and chemical shifts are reported with respect to tetramethylsilane as an internal standard. IR spectra were recorded on a Perkin-Elmer model 298 spectrometer. Mass spectra were obtained with a Hitachi-Perkin-Elmer model RMV-6E spectrometer. HPLC was performed with a Waters Associates model ALC 100 Analytical Liquid Chromatograph on a Waters μ Porasil (10μ silica) 3.9 mm x 30 cm column using a refractive index detector. The eluent was 5% (by volume) tetrahydrofuran in heptane. The liquid chromatograph was operated at a pressure of 325 psi at 40% of the maximum flow rate. Melting points were measured in open capillary tubes and are uncorrected.

cis- and *trans*-2,5-Diacetoxytetrahydrofuran. - A 100 ml, three-necked flask was fitted with a thermometer, a condenser, a nitrogen inlet and a 50 mL addition funnel. Lead tetraacetrate (Eastman Organic Chemicals), 8.8g (20 mmols) and 30 mL of anhydrous (distilled from $LiAlH_4$) tetrahydrofuran (THF) were placed in the flask with a magnetic stirring bar. Tetrahydrofuran-2,5-dicarboxylic acid (either *cis*- or *trans*-) 1.6g (10 mmols) was dissolved in 30 mL of anhydrous THF and was added through the dropping funnel under nitrogen over a period of 5 min. to the well-stirred slurry of LTA. The opaque, orange suspension turned a light yellow and the temperature rose to about 30°. The mixture was refluxed for 1.5 hr. The white precipitate was removed by filtration and the filtrate was evaporated to give 1.24g (65%) of a yellow oil, bp. 70°/0.02 torr, lit.[4] 84°-86°/0.3 torr. HPLC showed two major peaks at retention volumes of 26.5 ± 0.5 mL (*trans*) and 33 ± 0.5 mL (*cis*) in a ratio (by triangulation) of 2:1. The NMR and IR spectra are virtually identical to those obtained below.

cis-2,5-Diacetoxytetrahydrofuran. - A solution of 2.2g (12 mmols) of *cis*-2,5-dihydrofuran[4,6] in 60 mL of methanol was hydrogenated over 10% Pd on carbon (0.1g) in a Parr shaker at 20 psi. Hydrogen uptake was rapid. The catalyst was filtered, the solvent was evaporated and the residue was distilled in vacuo, 86% yield. NMR($CDCl_3$): δ 2.03 (6H, CH_3), 2.17 (4H, m, β-ring), 6.30 (2H, m, α-ring); IR(neat): 3000, 2960, 1750, 1370, 1235, 1115, 1060, 845 cm^{-1}; mass spectrum [70 eV, m/e (rel. int.)]: No parent ion, 160(21), 145(36), 129(14), 86(21), 84(32), 69(54), 43(100). HPLC showed one peak which had a retention volume of 33.8 ± 0.5 mL.

REFERENCES

[†] Recipient of the Andrew P. Dunlop Fellowship sponsored by the Quaker Oats Foundation.

1. L. L. McCoy and A. Zagalo, J. Org. Chem., 25, 824 (1960).

2. a) J. A. Moore and J. E. Kelly, J. Polym. Sci., Polym. Lett. Ed., 13, 333 (1975).

   b) idem., Macromolecules, 11, 568 (1978).

3. D. Gagnaire and P. Monzeglio, Bull. Soc. Chim. France, 2, 474 (1965).

4. N. Elming and N. Clauson-Kaas, Acta Chem. Scand., 6, 535 (1952).

5. C. Barbier, D. Gagnaire and P. Vottero, Bull. Soc. Chim. France, 1968, 2330.

6. J. P. Jacobsen, J. T. Nielsen and K. Schaumburg, Acta Chem. Scand., 25, 2785 (1971).

7. J. A. Moore and J. E. Kelly, Org. Prep. Proced. Int., 4, 289 (1972).

8. J. D. Bacha and J. K. Kochi, J. Org. Chem. 33, 83 (1968).

(Received September 8, 1980; in revised form September 19, 1980)