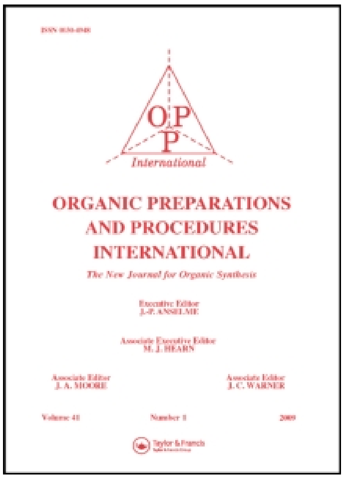

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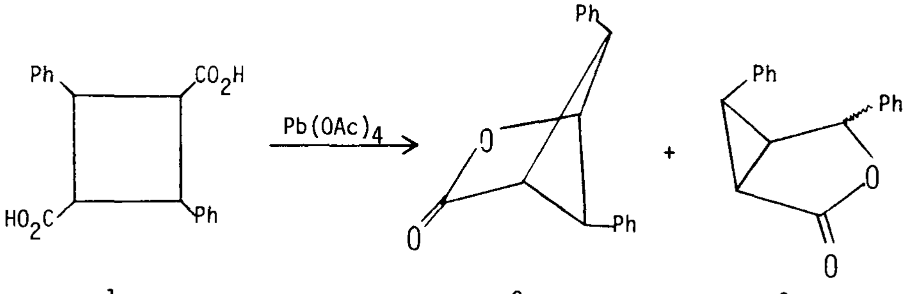

1 2 3

The lead tetraacetate oxidation of benzylic or tertiary 1,3-dicarboxylic acids to give γ-lactones has been reported.[1] We describe here an extension of this method to the preparation of the novel bicyclic lactone 2 in good yield from α-truxillic acid (1).[2] The ratio of the new lactone 2 to the known lactone 3[3] could be varied from 4:1 to 1:2.5 by the choice of solvent (see Table). The excess of 3 in acetic acid was not simply the result of rearrangement of 2 to 3, since 2 was not rearranged to 3 in lead tetraacetate in acetic acid. The stereochemistry of 2 was uniquely determined by the nmr data as assigned in the figure. Assignment of chemical shifts and coupling constants was made by the examination of a molecular model.

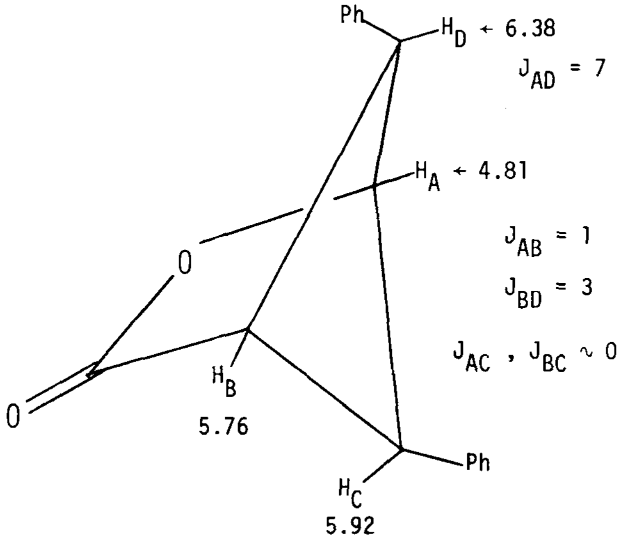

FIG.

Chemical Shifts (τ-values) and Coupling Constants (cps) in γ-Lactone **2**.

Experimental

Melting points are uncorrected in open capillaries. Spectra were obtained on a Perkin-Elmer Infracord infrared spectrophotometer, a JEOLCO C-60 H nmr spectrometer (TMS internal standard), and a Perkin-Elmer Hitachi RMU-6 mass spectrometer. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

Preparation of γ-Lactone **2**. A mixture of truxillic acid (10 g, 0.033 mole), commercial lead tetraacetate (46.6 g, 0.1 mole) and pyridine (15 ml) in dry benzene (250 ml) under a nitrogen atmosphere was placed in a 70-80° oil bath. A light yellow clear solution was formed. After 10 min., the solution started to become turbid and a precipitate formed. After 1.5 hr ethyl acetate (50 ml) was added and the reaction mixture was filtered. The filtrate was shaken with 200 ml of 3% sodium *meta* bisulfite and filtered free from the white precipitate of lead oxide. The organic layer was separated and shaken with 250 ml of 5% aq. sodium hydroxide to remove the unreacted truxillic acid. The organic layer (dried over magnesium sulfate) was evaporated to give 8.6 g of a yellow oily solid which was taken up in ether-hexane (90:10). Upon cooling, 4.8 g (57%) of 2 deposited; mp 173-174°; ir (Nujol) 1780 cm^{-1}; nmr τ ($CDCl_3$) 2.8 (s, 5H), 2.98 (m, 5H), 4.81 (dd, J_1 = 1.5 cps, J_2 = 7 cps, 1H), 5.76 (m, 1H), 5.92 (broad s, 1H), 6.38 (dd, J_1 = 7 cps, J_2 = 3 cps, 1H).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.59; H, 5.65; MW 250. Found: C, 81.50; H, 5.96; MW 250 (parent peak, mass spectrum).

Addition of hexane to the filtrate caused deposition of 2.1 g (25%) of 3. Recrystallization from hexane-ether (50:50) gave needles; mp 132-133° (lit.[3] 133°); ir (Nujol) 1770 cm^{-1}; nmr τ ($CDCl_3$) 2.7 (br s, 10H), 5.26 (br s, 1H), 7.4 (m, 3H).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.59; H, 5.65. Found: C, 81.75; H, 5.68.

Truxillic acid was treated with lead tetraacetate in acidic and neutral media. The following table summarizes the conditions and results of such experiments.

TABLE

Treatment of Truxillic Acid with Lead Tetraacetate in Various Solvent Systems

Run #	Truxillic acid, g (mole)	$Pb(OAc)_4$ g, (mole)	Time Hr	Solvent	Recovered acid, g	Total Yield	Ratio 2/3
1	8.88 (.030)	71 (.16)	5	ACOH 300 ml	3.7	32%	1.15/2.45
2	10 (.034)	50 (.11)	5	Benzene 600 ml	5.5	16%	2.5/1
3	5 (.017)	32[a] (.072)	5	Benzene 400 ml	0.9	45%	4/1

[a] Lead tetraacetate recrystallized from acetic acid and dried in the dark.

Attempted isomerization of lactone 2 to lactone 3. A mixture of 200 mg (0.0008 moles) of lactone 2, 1.7 gm (0.0036 moles) of lead tetraacetate (from a previously unopened bottle, prepd. 1/6/70), and 10 ml of glacial acetic acid was refluxed with stirring for 5 hrs. under nitrogen. The clear red solution (solution was clear yellow at beginning of reflux) was allowed to cool to room temperature. 10 ml of ethyl acetate was added, and the still clear red solution was filtered. Then, 10 ml of 3% $Na_2S_2O_5$ was added to the filtrate, and the mixture was shaken vigorously. The white precipitate of lead oxide was filtered, and 10 ml of water was added to the clear orange organic layer. Then, the mixture was shaken with 5% aq. potassium carbonate (2 x 30 ml), dried over Drierite, and evaporated to give a yellow-orange oil (100 mg). The nmr spectrum exhibited all the peaks characteristic of lactone 2, and none of the peaks characteristic of lactone 3.

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