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### A SIMPLE PREPARATION OF TRAUMATIC LACTONE. A PROSTANOID SYNTHON

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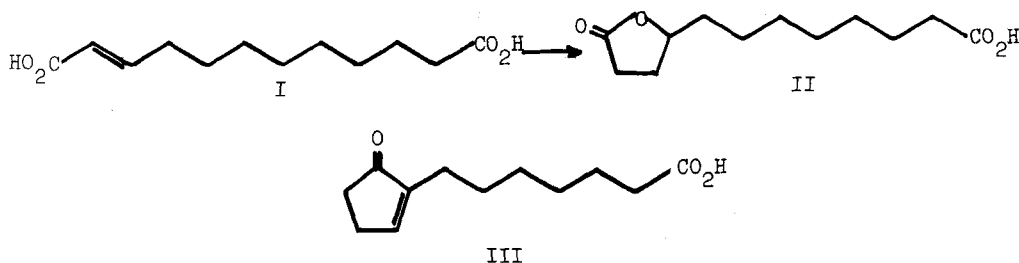
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A SIMPLE PREPARATION OF TRAUMATIC  
LACTONE<sup>†</sup>. A PROSTANOID SYNTHON

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(6/30/77)

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The importance of traumatic lactone(II) has recently been demonstrated<sup>1</sup> by its conversion with polyphosphoric acid, to the versatile prostaglandin synthon III. The reported conversion<sup>1</sup> of traumatic acid (I) to traumatic lactone(II) in 55% by heating with dilute H<sub>2</sub>SO<sub>4</sub> (concentration unspecified) has proved to be quite unsatisfactory. This transformation (I → II) has been achieved by treatment of molten I<sup>2</sup> with *p*-toluenesulfonic acid; the product was isolated as its methyl ester.



EXPERIMENTAL

All mps and bps are uncorrected. Light petroleum refers to the fraction, bp. 60-60°. The following instruments were used for spectral/analytical data: Perkin-Elmer Infracord model 137-E (IR); Varian Associates T-60 spectrometer (PMR: TMS as internal standard); CEC mass spectrometer model 21-110B (mass; 70 eV, direct inlet system). "Aerograph" model A-350-B (10% silicone SE-30 on chromosorb W of 60-80 mesh, H<sub>2</sub> as carrier gas; temp. 200°).

Methyl ester of traumatic lactone.- Traumatic acid<sup>2</sup> (22.8 g, 0.1 mole) and *p*-toluenesulfonic acid (2.28 g) were mixed in a flask fitted with an air condenser and heated in an oil bath at 200 ± 5° (silica gel guard tube). After 6 hrs (optimized), the reaction mixture was cooled treated with dry

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methanol (220 ml) and left overnight at room temperature for 16 hrs. The product was isolated in the usual manner and the crude ester (24.5 g) (TLC: solvent 10% EtOAc in  $C_6H_6$ , 2 major spots) was chromatographed on  $SiO_2$  gel (gr. II, 650 g, 92 x 4.5 cm) with TLC monitoring of fractions.

Fraction 1	light petroleum	500 ml x 4	0.24 g	mixture
Fraction 2	$C_6H_6$	500 ml x 2	1.03 g	mixture
Fraction 3	$C_6H_6$	500 ml x 2	2.24 g	pure; nonconjugated isomer of I (dimethyl ester)
Fraction 4	10% EtOAc in $C_6H_6$	500 ml x 6	14.34 g	pure II as methyl ester
Fraction 5	50% EtOAc in $C_6H_6$	500 ml x 6	3.20 g	pure II as methyl ester

Fractions 4 and 5 were mixed and distilled to furnish the methyl ester of traumatic lactone as a colorless liquid (solidifies in the refrigerator), bp. 178-180°/0.5 mm (15.6 g, 65%); IR (smear):  $\nu_{max}$  1770, 1730 and 1180  $cm^{-1}$ ; nmr ( $CCl_4$ ):  $\delta$  3.60 (s, 3H,  $COOCH_3$ ), 4.30 (br m, 1H,  $-O-\underset{CH_2}{\underset{|}{CH}}-CH_2$ ); Mass: m/e 242 (0.2%), 211 (M-OCH<sub>3</sub>, 7%), 85 (100%).<sup>3</sup>

Anal. Calcd. for  $C_{13}H_{22}O_4$ : C, 64.44; H, 9.15.

Found: C, 65.06; H, 8.90.

Fraction 3 was colorless liquid, bp. 130-133°/0.5 mm (2.06 g, ca 8%); IR (smear):  $\nu_{max}$  = 1730, 1639 and 970  $cm^{-1}$ ; nmr( $CCl_4$ ):  $\delta$  3.60 (s, 6H, 2 x  $COOCH_3$ ), 5.33 (br m, 2H,  $H_2C-\underline{CH}=\underline{CH}-CH_2$ ); Mass: m/e  $M^+$  256 (24%), 692 (100%).

Anal. Calcd for  $C_{14}H_{24}O_4$ : C, 65.59; H, 9.44.

Found: C, 65.53; H, 9.48.

The ester (4.84 g 0.02 mole) and a 10% aqueous alcoholic potassium hydroxide solution (40 ml) were refluxed for 4 hrs. Most of the ethanol was removed under reduced pressure and the residue was diluted with water (100

ml) and extracted with ether to remove any neutral material. The alkaline aqueous layer was acidified with hydrochloric acid (Congo red), extracted with ether (100 ml x 3), washed with water, dried and the solvent removed. Distillation of the residue yielded 3.34 g (73%) of II as a colorless liquid, bp. 195-198°/0.4 mm which solidified, mp. 48-50°, lit.<sup>1</sup> bp. 190-195°/0.4 mm, IR (CHCl<sub>3</sub>):  $\nu_{\max}$  3200, 2680, 1770, 1705 and 1180 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>):  $\delta$  4.43 (broad m, 1H,  $-\text{O}-\underset{\text{CH}_2}{\text{CH}}-\text{CH}_2$ ).

Anal. Calcd. for C<sub>12</sub>H<sub>20</sub>O<sub>4</sub>: C, 63.13; H, 8.83.

Found: C, 63.36; H, 9.17.

Esterification of II with CH<sub>2</sub>N<sub>2</sub> gave a product identical (TLC, IR, PMR) with the ester described earlier.

#### REFERENCES

- † The trivial name traumatic lactone has been adopted for dodecan-4-olide-12-oic acid, the lactone acid II (R = H) derived from traumatic acid I.
- †† Communication No. 2114, National Chemical Laboratory, Poona.
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