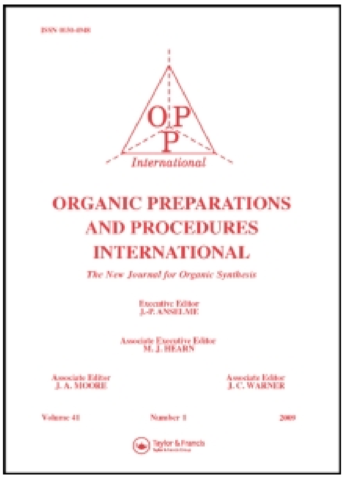

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β- AND δ-TRUXINIC ACIDS

M. Freedman[a]; Y. Mohadger[a]; J. Rennert[a]; S. Soloway[a]; I. Waltcher[a]
[a] Department of Chemistry, The City College of The City University of New York, New York

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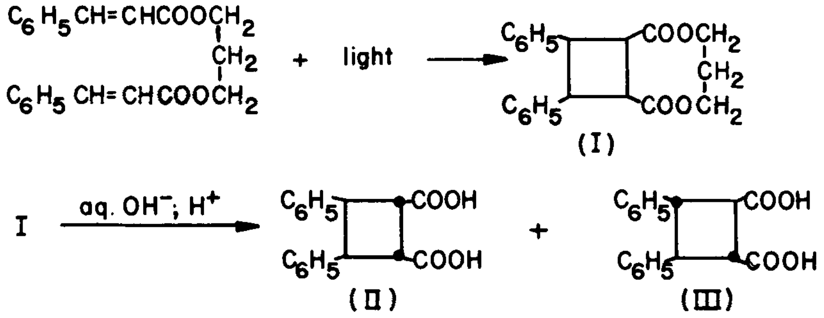
β- AND δ-TRUXINIC ACIDS

M. Freedman, Y. Mohadger, J. Rennert, S. Soloway and I. Waltcher
Department of Chemistry
The City College of The City University of New York, New York 10031



The irradiation of unsensitized liquid trans-cinnamic acid derivatives or of solutions of trans-cinnamic acid or its derivatives does not give photodimerization products.[1,2] Solid state irradiation[3] below 50° of the less stable allotrope of trans-cinnamic acid, the β-form, does yield β-truxinic acid (II). However, the difficulty of preparing the pure β-allotrope and its easy conversion to the more stable α-form makes this route to pure (II) an inconvenient one.

δ-Truxinic acid (III) has been reported[4] as the product of the photodimerization of dibenzylideneacetone in benzene-isopropanol solution followed by oxidation of the diketone dimer, but this isomer has never been reported as a product of the photodimerization of cinnamic acid or its derivatives.

In our laboratory recent studies have shown that irradiation of α,ω-polymethylene dicinnamates in dilute solution results in intramolecular cyclization as illustrated by the product (I). The stereochemistry of the bridged cyclobutane esters that are obtained appears to be dependent on the length of the polymethylene chain. Thus, irradiation of the 1,3-trimethylene dicinnamate gave a mixture of two readily separable esters with one yielding β-truxinic acid on hydrolysis and the other giving the δ-isomer. On the other hand, irradiation of 1,4-tetramethylene dicinnamate resulted in only one product which gave δ-truxinic acid on hydrolysis.

Experimental

1,3-Trimethylene dicinnamate. A solution of 38 g. (0.50 mole) of trimethylene glycol, 148 g. (1.0 mole) trans-cinnamic acid, and 10 g. p-toluenesulfonic acid in 150 ml. toluene was refluxed for three hours after which toluene and water were slowly distilled off until the thermometer recorded the boiling point of toluene. On cooling, the contents of the flask solidified. The material was taken up in 300 ml. of chloroform, extracted successively with aqueous bicarbonate and with water, and the solvent was removed to give 164 g. of crude product. Two recrystallizations from methanol yielded 142 g. (85%) of product, m.p. 87-88°. IR spectrum (KBr): 1730 (s), 1650 (m), 1190 (s), 1170 (s), 760 (s), 710 (s).

Analysis:	Calcd.	C, 74.98	H, 5.99
$C_{21}H_{20}O_4$	Found	C, 75.27	H, 6.08

Photocyclization Products. A quartzware flask containing a 1% solution of 3.0 g. of 1,3-trimethylene dicinnamate in refluxing cyclohexane was irradiated for one week using a 275 watt "sunlamp" as a light source. On cooling, 0.2 g. of a white solid separated, m.p. 271-272°. IR spectrum (KBr): 1720(s), 1260(s), 1065(m), 750(m), 690(s).

Analysis	Calcd.	C, 74.98	H, 5.99
$C_{21}H_{20}O_4$	Found	C, 74.80	H, 5.87

Saponification of this bridged cyclobutane diester followed by acidification gave the known δ-truxinic acid in nearly quantitative amounts.

Evaporation of the cyclohexane gave an oily residue from which 1.7 g. of crystals was obtained whose crystallization was induced by stirring briskly with 10 ml. of a 1:1 ether-petroleum ether solution. Recrystallization from methanol gave 1.7 g. of a colorless solid, an isomer of (I), m.p. 162-163°. IR spectrum (KBr): 1720(s), 1250(s), 1180(s), 1060(m), 750(m), 690(s).

Analysis:	Calcd.	C, 74.98	H, 5.99
$C_{21}H_{20}O_4$	Found	C, 75.16	H, 6.01

Saponification of this isomer gave β-truxinic acid quantitatively. The total of the weights of the two esters was 1.9 g. (63%).

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