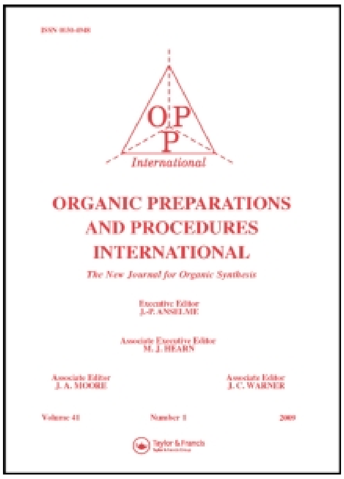

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SYNTHESIS OF *cis*-4-OCTENE-1,8-DIOIC ACID AND ITS ESTERS

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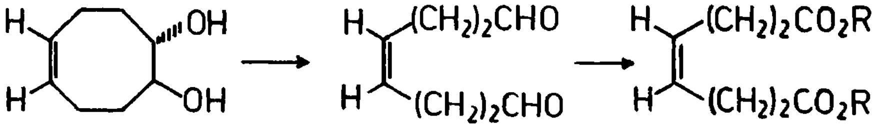
While methods for the synthesis of *trans*-4-octene-1,8-dioic acid (*trans*-IIIa) and of its esters (*trans*-IIIb,c) have been described in detail,[1,2] the preparation of the title compound by ozonolysis of *cis*,*cis*-1,5-cyclooctadiene is only outlined in the literature without experimental details or characterization.[3,4] We now describe a convenient synthesis of *cis*-IIIa and its esters (*cis*-IIIb and IIIc), starting from *cis*-5-cyclooctene-*trans*-1,2-diol (I), readily obtainable from *cis*,*cis*-1,5-cyclooctadiene.[5] The diol I was oxidized by sodium metaperiodate in THF-water to the dialdehyde II and thence, without further purification with Jones' reagent to *cis*-IIIa in 50% overall yield.



I II III

a) R = H b) R = CH_3 c) R = $C(CH_3)_3$

A method for the conversion of cis,cis-1,5-cyclooctadiene into II was developed recently.[6] The transformation of II into the acid IIIa provide further evidence that the cis configuration of the double bond in the starting material was retained during the synthetic sequence.

EXPERIMENTAL

cis-4-Octene-1,8-dialdehyde (II).- A solution of sodium metaperiodate (25.7 g. 0.12 mole) in water (150 ml.) was added dropwise to a well stirred and ice-cooled solution of the diol I (14.2 g. 0.1 mole) in THF (150 ml.). The reaction mixture was stirred for an additional 24 hrs. at room temperature and the precipitated solid was filtered. The filtrate was saturated with brine and the product extracted with five 100 ml. portions of ether. After the usual work-up, the liquid residue was utilized in the next step without purification. The dialdehyde was characterized as its bis-2,4-dinitrophenylhydrazone, mp. 173° (from ethyl acetate). I.R. (neat): ν_{max} 1720 cm^{-1}.

Anal. Calcd. for $C_{20}H_{20}N_8O_8$: C, 48.00; H, 4.02; N, 22.39.
Found: C, 48.06; H, 4.11; N, 22.27.

cis-4-Octene-1,8-dioic acid (IIIa) and its esters (IIIb) and (IIIc).- Jones' reagent[7] was added to a solution of the crude dialdehyde II in acetone (400 ml.), cooled to -10° until a reddish color persisted. After quenching of excess of oxidant with ethyl alcohol, anhydrous magnesium sulphate was added and the green mixture filtered through Celite. Removal of the solvents in vacuo gave the solid acid (7 g.), which was crystallized from a 1:4 mixture of benzene-petroleum ether (bp. 40-70°). An analytical sample was obtained by crystallization from a 1:7 mixture of ethyl ether-petroleum ether (bp. 40-70°) mp. 97-98°. I.R. (nujol): ν_{max} 1700 cm^{-1}.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03.
Found: C, 55.70; H, 6.92.

The methyl ester IIIb was prepared by allowing to stand for 24 hrs. at room temperature a solution of 3.44 g. (0.02 mole) of the acid IIIa in 50 ml. of absolute methanol containing 2 ml. of concentrated sulfuric acid. The mixture was neutralized with saturated sodium bicarbonate solution, most of the methanol evaporated in vacuo and the residue extracted with five 30 ml. portions of ether. The extract was washed with water, dried over anhydrous magnesium sulfate and evaporated to give 3.4 g. (85%) of the ester IIIb, bp. 75°/0.01 mm. identical with a sample obtained by action of ethereal diazomethane on IIIa.
I.R. (neat): ν_{max} 1730 cm^{-1}.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05.
Found: C, 59.85; H, 8.01.

The t-butyl ester IIIc was prepared in a pressure bottle charged with dichloromethane (60 ml.) and 0.3 ml. of concentrated sulfuric acid. The solution was cooled with an ice-salt bath to 0°, and 3.44 g. (0.02 mole) of the acid IIIa and approximately 25 g. of isobutylene were added. The bottle was closed and shaken mechanically at room temperature overnight. The bottle was chilled in ice-salt bath and then opened. The reaction mixture was carefully poured into 10% sodium hydroxide solution (60 ml.). The layers were separated and the aqueous portion was extracted with two 50 ml. portions of dichloromethane. The extract was dried over anhydrous magnesium sulfate and evaporated to give 5 g. (89%) of the ester IIIc, mp. 58-59° (from petroleum ether 40-70°) A mixture mp. with <u>trans</u>-IIIc was lowered.

I.R. (nujol): ν_{max} 1730 cm^{-1}.

<u>Anal</u>. Calcd. for $C_{16}H_{28}O_4$: C, 67.60; H, 9.85.

Found: C, 67.52; H, 9.79.

Both the esters on alkaline hydrolysis give the starting acid.

REFERENCES

1. R. Lukes, Chem. Listy, <u>52</u>, 1926 (1958), C.A. <u>53</u>, 3055c (1959).
2. K. Sisido, K. Sei and H. Nozaki, J. Org. Chem., <u>27</u>, 2681 (1962).
3. R. H. Perry Jr., Amer. Chem. Soc. Div. Petrol. Chem. Preprints 12(2) D-5 D-10 (1967), C.A. <u>68</u>, 12407c (1968).
4. M. I. Fremery and E. K. Field, J. Org. Chem., <u>28</u>, 2537 (1963),
   E. K. Field, World Petrol. Congr. Proc. 7th (1967), C.A. <u>71</u>, 60374a (1969).
5. P. Yates, E. G. Lewards and P. H. McCabe, Can. J. Chem., <u>50</u>, 1548 (1972).
6. J. P. Nagarkatti and K. R. Ashley, Tetrahedron Lett., 4599 (1973).
7. C. Djerassi, R. R. Engle and A. Bowers, J. Org. Chem., <u>21</u>, 1547 (1956).

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