Substituent Effects on the Oxymercuration–Demercuration of Long-chain Unsaturated Esters

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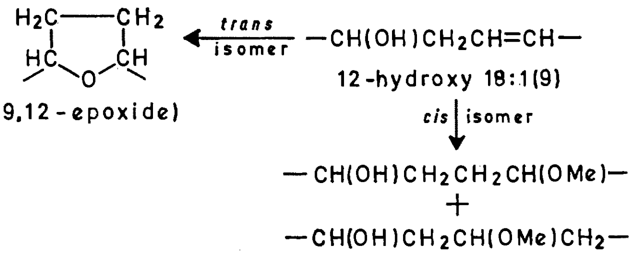
Summary In the oxymercuration–demercuration of long-chain unsaturated esters the presence of a substituent (OH, OMe, OAc) affects the proportion of the two isomeric products and, in some cases, furnishes novel products through interaction of the substituent with the intermediate mercury compound.

Methoxymercuration–demercuration has long been used as a means of separating long-chain esters differing in unsaturation[1] and, more recently, as a method of "labelling" double bonds prior to m.s. examination.[2] Its use as a preparative procedure has hardly been exploited and we report some useful and interesting results.

Methyl oleate gave a 1 : 1 mixture of methyl 9- and 10-methoxystearates in high yield (98%) when treated first with mercury(II) acetate and methanol followed by *in situ* reduction by sodium borohydride. When methanol was replaced by ethanol (ethoxy), acetic acid (acetoxy), or water–tetrahydrofuran (hydroxy) the appropriate esters were obtained, still as 1 : 1 mixtures in high yield (87—96%) and sometimes accompanied by a little starting material. In a similar way methyl linoleate gave a mixture of methyl dimethoxystearates (80%), but methyl hendec-10-enoate gave only one product: methyl 10-methoxyhendecanoate (86%).



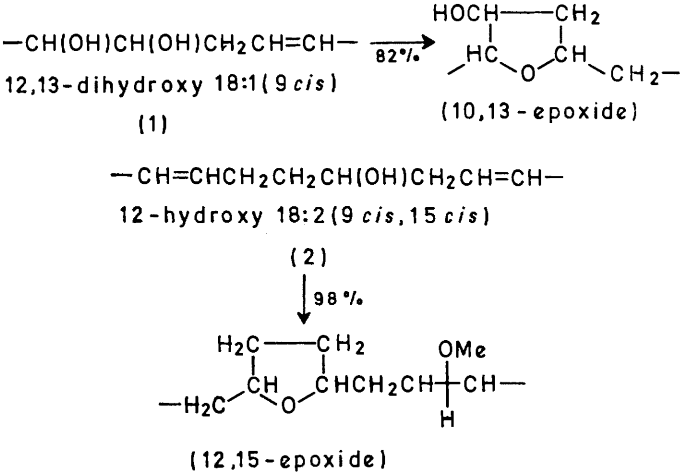
SCHEME

Methyl 12-hydroxyoleate (ricinoleate) and methyl 9-hydroxyoctadec-*cis*-12-enoate and their *trans*-isomers were used as a source of the corresponding acetoxy- and methoxy-octadecenoates. These esters have an additional functional group (OH, OAc, or OMe) β or γ to the double bond and we have used them to confirm and extend the work of Henbest and Nicholls[3] on related compounds of lower molecular weight. Our results (see Table) show that with the methoxy- and acetoxy-alkenoates there is little difference between the *cis*- and *trans*-isomers and that the two isomeric products are formed in different amounts. Three of the hydroxy alkenoates gave high yields of tetrahydrofurans (9,12-epoxides) (see Scheme) but with methyl ricinoleate the hydroxyl group is only slightly involved in this way.

Products of methoxymercuration–demercuration

Substrate		Product (area % on g.l.c.)		9,12-epoxide	
		9-OMe	10-OMe	*trans*	*cis*
12-OMe	18 : 1(9 *cis*)	79	18	—	—
12-OMe	18 : 1(9 *trans*)	70	17	—	—
12-OAc	18 : 1(9 *cis*)	70	18	—	—
12-OAc	18 : 1(9 *trans*)	60	10	—	—
12-OH	18 : 1(9 *cis*)	66	18	8	2
12-OH	18 : 1(9 *trans*)	—	—	17	82
				9,12-epoxide	
		12-OMe	13-OMe	*trans*	*cis*
9-OMe	18 : 1(12 *cis*)	*ca.* 41	*ca.* 56	—	—
9-OMe	18 : 1(12 *trans*)	*ca.* 38	*ca.* 59	—	—
9-OAc	18 : 1(12 *cis*)	*ca.* 31	*ca.* 66	—	—
9-OAc	18 : 1(12 *trans*)	*ca.* 32	*ca.* 64	—	—
9-OH	18 : 1(12 *cis*)	—	—	31	67
9-OH	18 : 1(12 *trans*)	—	—	31	60

The difference between β- and γ-hydroxy *cis*-alkenes is reflected in the products of methoxymercuration–demercuration of methyl 12,13-dihydroxyoleate (**1**) and of methyl 12-hydroxyoctadeca-*cis*-9,*cis*-15-dienoate (densipolate, **2**).



Using methyl octadecenoates with the double bond near to the methoxycarbonyl function we have shown that the ester group also has a strong influence on the proportion of the two possible products.

A typical reaction procedure was as follows. The unsaturated ester (*ca.* 50 mg) was dissolved in dry methanol or other solvent (5 ml). Mercury(II) acetate (1·0 mole excess) was added and the solution was stirred at room temperatures for 2—4 days. The solution was then cooled to 0° and stirred during addition of an excess of sodium borohydride in water (10 ml) and thereafter at room temperature for a further 30 min. The product was recovered by partition between ether and water saturated with sodium chloride and examined by g.l.c. (using 5 ft. packed or 50 m capillary columns with diethyleneglycol succinate as stationary phase). Individual components were separated by preparative t.l.c. (silica) and identified by m.s.

We thank the S.R.C. for a Research Studentship and Dr. G. Fuller (U.S. Dept. of Agriculture, Albany, California) for the gift of methyl densipolate.

(*Received, May 27th,* 1970; *Com.* 800.)

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