

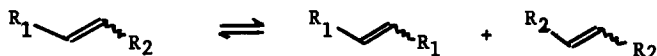
THE TUNGSTEN CATALYSED METATHESIS OF ω -OLEFINIC ESTERS

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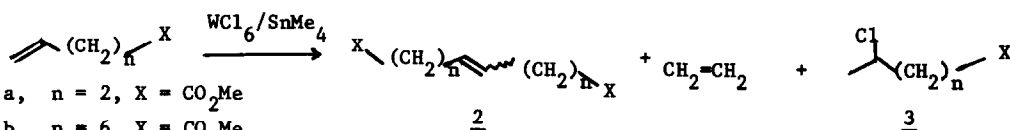
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Olefin metathesis catalysed by transition metal complexes is a fascinating and potentially extremely useful reaction involving the exchange of alkylidene groups between olefins.^{1,2.}



Mechanistic investigations have implicated a variety of possible intermediates and only recently has firm experimental evidence been presented to show that metallocarbenes are the most likely active precursors.² The number of examples involving the metathesis of functionalised olefins is very small. Methyl oleate has been metathesised using a $WCl_6 - SnMe_4$ system to a mixture of octadec-9-ene and the dimethyl ester of octadec-9-enedioic acid³. In the present communication we report the metathesis of a series of ω -olefinic esters which proceed with the elimination of ethylene to give a stereoisomeric mixture of diester olefins whose cis: trans ratio is in accord with thermodynamic considerations.



1. a, $n = 2$, $X = CO_2Me$
- b, $n = 6$, $X = CO_2Me$
- c, $n = 8$, $X = CO_2Me$
- d, $n = 8$, $X = CH_2OAc$

The olefinic esters (1) were treated in chlorobenzene at 70° for 16h. with a catalyst mixture prepared from WCl_6 and $SnMe_4$. In all cases the major product was that from metathesis (2) while some 10% arose by addition of HCl across the terminal double bond (3) (Table). The stereochemistry of the dimethyl esters 2a, b and c was studied by the use of CMR of the product mixtures and g.l.c. analysis of the derived epoxides. Typically, epoxidation of 2a was achieved in >90% yield by reaction with m-chloroperbenzoic acid in CH_2Cl_2 at 0°. G.l.c. analysis (5', 3% Carbowax 20M, Diatomite C, 60-80 mesh) indicated the presence of two components in the ratio 75:25. The peak of smaller area was assigned to the cis-epoxide since the I.R. of the olefinic mixture showed a strong absorption at 970 cm^{-1} but no absorption at 670-730 cm^{-1} . The major component of the mixture of epoxides had the shorter

TABLE
Metathesis of ω -olefinic esters, WCl_6-SnMe_4 in $PhCl$, 68° *

Reactant	% Conversion	Product Composition (%)	
		<u>2</u>	<u>3</u>
1a	41	83	17
1b	40	93	7
1c	54	85	15
1d	35	90	10

* $WCl_6:SnMe_4$: olefin = 1:1.35:20; 16h reaction.

retention time on g.l.c. analysis which is consistent with the previous observations that trans-epoxides have a shorter retention time than their cis-analogues.⁴

The isomer ratio of the products has also been studied by CMR, employing a long delay time to allow the relaxation of the carbon nuclei*. This procedure enabled an estimate of the relative proportion of the isomeric products to be made by integration. Thus for 2a, two absorptions were observed at 129.18 and 129.63 ppm[‡] and the former was attributed to the cis-vinyl carbon; the integrals observed were then consistent with a ratio of trans:cis of 80:20. These data are fully in agreement with the conclusion based on g.l.c. analysis of the epoxide mixture. Similarly for 2b, peaks at 129.88 and 130.38 ppm were attributed to the cis and trans-vinyl carbons respectively, leading to the conclusion that the mixture consisted of a 59:41 ratio of trans:cis isomers. Confirmation of this by g.l.c. analysis proved difficult since, although broad peaks could be obtained, complete separation was not possible.[†] Only one absorption was observed in the CMR of 2c at 130.42 ppm but since peaks at 960 and 725 cm^{-1} were apparent in the I.R. spectrum, it can be suggested that the cis- and trans-vinyl carbons resonate in identical positions.

The ratios found are in agreement with the formation of mixtures of products reflecting thermodynamic factors. The efficient use of these reactions in synthesis could therefore be limited to those cases where formation of a cis, trans mixture is desirable, e.g. in the formation of some insect pheromone mixtures.

* Four second delay employed

‡ relative to TMS

† due to the high-boiling character of the products polar columns could not be employed.

1. N. Calderon, Acc. Chem. Res., 1972, 5, 127; W.B. Hughes, Organomet synth. 1972, 1, 341.
2. T.J. Katz and R. Rothchild, J. Amer. Chem. Soc., 1967, 98, 2519 and others.
3. P.B. Van Dam, M.C. Mittelmeijer and C. Boelhouwer, J. Chem. Soc. Chem. Commun., 1972, 1221.
4. L.M. Donough and D.A. George, J. Chromatogr. Sci., 1970, 8, 158.