

Heterogeneous Metathesis of Alkenes having Functional Groups

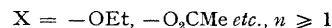
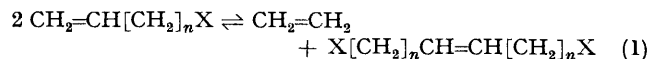
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Summary Various alkenes carrying functional groups are metathesized, with a high selectivity, with the catalyst system $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$, promoted by a small amount of tetramethyltin.

THE metathesis of alkenes carrying heteroatom functional groups constitutes one of the most promising synthetic applications of the metathesis reaction. In recent years some reports have been made of the homogeneously catalysed metathesis of acyclic functionally substituted alkenes (although sometimes with very low conversion and low selectivity), *e.g.* unsaturated fatty acid esters,¹ unsaturated ethers,^{2,3} and nitrogen-containing unsaturated compounds.^{3,4} In the field of heterogeneously catalysed metathesis, the catalyst rhenium heptoxide on alumina, to which a small amount of tetramethyltin is added, was found to be an active catalyst for the metathesis of unsaturated fatty acid esters.⁵ Here we report that with this catalyst system other heteroatom-containing alkenes can also be metathesized, such as unsaturated ethers and ketones, alkenyl esters, and halogeno-alkenes.

The reactions were carried out in the liquid phase in a stirred glass batch reactor at room temperature. The $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ catalyst was prepared and activated as described earlier.⁵ After activation the catalyst (500 mg, 17% Re_2O_7 by weight) was introduced into the reactor under nitrogen, followed by CCl_4 (2 ml), Me_4Sn (5 μl ; 0.036 mmol), and the alkene (0.25 ml). Ethene was formed immediately, in accordance with reaction (1). The conversion was



followed by measuring the ethene concentration in the gas phase. After the ethene formation was completed (reaction time *ca.* 6 h), the solid catalyst material was separated from the liquid phase. The liquid phase was analysed by g.l.c. (2 m \times $\frac{1}{4}$ in column, 3% Carbowax 20 m on Chromosorb P-AW, 60-80 mesh, 2 min hold at 80 °C, then with 30 °C min^{-1} to 180 °C, N_2 carrier, flame ionisation detector). The reaction products were identified by n.m.r.

and mass spectroscopy. Typical examples of reactions with various oxygen-containing alkenes are given in the Table. The selectivity to the primary metathesis products

TABLE. Metathesis of oxygen-containing alkenes catalysed by $\text{Re}_2\text{O}_7(+\text{Me}_4\text{Sn})-\text{Al}_2\text{O}_3$ at room temperature.^a

Reactant	Conversion/ mol %	Selectivity/ mol %	<i>trans</i> : <i>cis</i> Ratio of difunctional alkene
$\text{CH}_2=\text{CHCH}_2\text{OEt}$	40	98	2.6
$\text{CH}_2=\text{CHCH}_2\text{OC}(\text{:O})\text{Me}$	17	96	2.8
$\text{CH}_2=\text{CH}[\text{CH}_2]_2\text{C}(\text{:O})\text{Me}$	35	97	b

^a Conditions: see text. ^b N.m.r. spectroscopy showed a *trans/cis* mixture; however, the *cis*- and the *trans*-isomers were not resolved by g.l.c. under our conditions.

proved to be nearly 100%, which means that no double-bond isomerisation (and subsequent metathesis and/or polymerisation) had taken place.† In all cases, both the *cis* and the *trans* form of the difunctional alkene were obtained.

† With substituted alkenes having a relatively strong electron-attracting heterogroup double-bond isomerisation is highly favoured with our catalyst system. For instance, at room temperature allyl cyanide was rapidly transformed into crotonitrile, and no metathesis took place.

¹ P. B. van Dam, M. C. Mittelmeijer, and C. Boelhouwer, *J.C.S. Chem. Comm.*, 1972, 1221; R. Nakamura, S. Fukuhara, S. Matsumoto, and K. Komatsu, *Chem. Letters*, 1976, 253; R. Baker and M. J. Crimin, *Tetrahedron Letters*, 1977, 441.

² W. Ast, G. Rheinwald, and R. Kerber, *Rec. Trav. chim.*, 1977, 96, M127.

³ R. Nakamura, S. Matsumoto, and E. Echigoya, *Chem. Letters*, 1976, 1019.

⁴ J. P. Laval, A. Lattes, R. Mutin, and J. M. Basset, *J.C.S. Chem. Comm.*, 1977, 502; R. Nougier, R. Mutin, J. P. Laval, G. Chapelet, J. M. Basset, and A. Lattes, *Rec. Trav. chim.*, 1977, 96, M91.

⁵ E. Verkuijlen, F. Kapteijn, J. C. Mol, and C. Boelhouwer, *J.C.S. Chem. Comm.*, 1977, 198.

⁶ G. S. Lewandos, Ph.D. Thesis, University of Texas at Austin, 1972, p. 60.

⁷ R. A. Fridman, A. N. Bashkurov, L. G. Liberov, S. M. Nosakova, R. M. Smirnova, and S. B. Verbovetskaya, *Doklady Akad. Nauk S.S.S.R.*, 1977, 234, 1354.

It is noteworthy that the homogeneously catalysed metathesis of unsaturated ethers appears to be possible only when the oxygen atom is separated from the carbon-carbon double bond by at least two methylene groups ($n \geq 2$).³ This would mean that, *e.g.*, allyl ethyl ether does not react homogeneously. Also attempted homogeneously catalysed metathesis of allyl acetate was not successful.⁶

With our catalyst system halogen-containing alkenes could also be converted into their metathesis products. For instance, under the applied conditions, allyl bromide reached *ca.* 50% conversion within 30 min (selectivity 93%). The metathesis of low-molecular weight halogen-substituted alkenes is in agreement with recent results obtained with a similar catalyst.⁷ However, it has been reported that these halogeno-alkenes do not metathesise homogeneously.³

The suitability of our heterogeneous catalyst system for the metathesis of various substituted alkenes offers new routes to difunctional compounds, *e.g.* 1,4-diacetoxybut-2-ene, which are important intermediates for the synthesis of products of technological interest.

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