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HIGH-YIELD CATALYTIC METATHESIS OF ALKENYL TOSYLATES WITH APPLICATIONS IN ORGANIC SYNTHESIS

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Summary Alkenyl tosylates of the type $RCH=CH(CH_2)_nOTs$ [R=H, n=9; R=H, n=7; and $R=CH_3(CH_2)_7$, n=8] undergo metathesis using a WCl_6-Me_3SnCl catalyst system, producing difunctionalised alkenes of the type $TsO(CH_2)_nCH=CH(CH_2)_nOTs$ (n=7,8, and 9); examples of the use of these products in synthesis are presented.

Despite much progress over the past ten years in elucidating the mechanism of catalytic olefin metathesis,[1] the reaction has not yet joined the repertoire of organic chemistry as a synthetically useful routine. Whereas many examples exist of its application to simple alkenes, much less information is available for alkenes with additional heteroatom functional groups, the area of its greatest potential in organic synthesis. The chief difficulty appears to be that most catalyst systems are easily poisoned by polar functional groups. However, some metathesis studies with alkenyl esters[2] and nitriles[3] have been successful, but product yields are generally low and in some instances are difficult to reproduce. In an effort to make the metathesis reaction more generally useful in organic synthesis we have screened a range of functional groups attached to the 11-position of 1-undecene using a tungsten hexachloride-trimethyltin chloride catalyst system. The most promising group to emerge thus far is the tosylate group. 11-Undecenyl tosylate (1)[4] and WCl_6/Me_3SnCl in chlorobenzene produced a cis,trans mixture of metathesis products in 98% yield using the following procedure.

To the tosylate (1) (2.0g) in dry chlorobenzene (13 ml) was added trimethyltin chloride (0.62g). The solution was stirred at 60^oC and tungsten hexachloride (0.12g) was added. The mixture was kept at 60^oC for 24h, then was cooled and diluted with hexane (20 ml). Dry ammonia was bubbled through the mixture for 5 min. Filtration and concentration of the filtrate at reduced pressure gave an oil which on column chromatography (silica gel,$CHCl_3$) gave 1.94g (98%) of 10-eicosenyl-1,20-ditosylate (2).[5] The product consisted of approximately

(1) $CH_2=CH(CH_2)_9OTs$
(2) $TsO(CH_2)_9CH=CH(CH_2)_9OTs$
(3) $CH_2=CH(CH_2)_7OTs$
(4) $TsO(CH_2)_7CH=CH(CH_2)_7OTs$
(5) $CH_3(CH_2)_7CH=CH(CH_2)_8OTs$
(6) $CH_3(CH_2)_7CH=CH(CH_2)_7CH_3$
(7) $TsO(CH_2)_8CH=CH(CH_2)_8OTs$
(8) $CH_3(CH_2)_8CH=CH(CH_2)_8CH_3$
(9) $TsO(CH_2)_{20}OTs$
(10) $NC(CH_2)_9CH=CH(CH_2)_9CN$
(11) $NC(CH_2)_{20}CN$
(12) $TsO(CH_2)_{10}OH$

equal amounts of the cis and trans isomers. This simple procedure was also used to convert 9-nonenyl tosylate (3)[4] into 8-hexadecenyl-1,16-ditosylate (4)[5](80%) and oleyl tosylate (5)[4] into a separable mixture of 8-octadecene (6) (40%) and 9-octadecenyl-1,18-ditosylate (7)[5] (40%), products in each case consisting of cis and trans isomers.

Efficient metathesis of alkenyl tosylates is particularly useful in organic synthesis because of the ease with which the tosylate group can be introduced and subsequently transformed into other functional groups. The metathesis reactions reported here open up simple routes to a variety of molecules. For example, lithium aluminium hydride reduction of (2) gave cis- and trans-10-eicosene (8)[5] (88%). Hydrogenation of (2) over palladium gave eicosanyl-1,20-ditosylate (9)[5](98%). Treatment of (2) with sodium cyanide in DMSO produced cis- and trans-1,20-dicyano-10-eicosene (10)[5] and the same combination of reagent and solvent converted the saturated ditosylate (9) into 1,20-dicyanoeicosane (11).[5] Ozonolysis of (2) followed by sodium borohydride reduction produced the monotosylate of 1,10-decanediol (12).[5]

The application of alkenyl tosylate metathesis to the synthesis of cycloalkenes is under investigation.

References

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4. Prepared from the commercially available alcohol and tosyl chloride in pyridine.
5. All new compounds gave ^1H and ^{13}C n.m.r. data consistent with the assigned structures and satisfactory combustion and/or mass spectrometric analysis.
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