Metathesis of Olefins Having a Quaternary Ammonium Group

By JEAN-PAUL LAVAL and ARMAND LATTES*
(*Laboratoire des composés azotés polyfonctionnels Université Paul Sabatier, Toulouse, France*)
and ROBERT MUTIN and JEAN MARIE BASSET
(*Institut de Recherche sur la catalyse* 79, *Boulevard du* 11 *novembre* 1918 69626 *Villeurbanne Cédex, France*)

Summary Whereas metathesis of olefins with primary or tertiary amino groups is ineffective with conventional catalysts, metathesis of olefins with quarternary ammonium groups results in α–ω bifunctional olefins.

METATHESIS of acyclic and cyclic olefins has been intensively investigated in the last decade[1] but this reaction has seen limited use, so far, in organic[2] or organometallic synthesis[3] probably owing to catalyst poisoning by most functional groups. We report data which indicate that olefins with amino groups are inactive for metathesis but become active when the amine function is quaternised.

TABLE. Metathesis of the olefins (I)—(IV) containing amino or ammonium groups.

Olefin	Catalyst system[a]	% Selectivity	% Conversion after 2 h	*trans* : *cis* ratio of C_4[b] product
(I)	(A)	—	0	—
(II)	(A)	—	0	—
(III)	(A)	75	11	—
(IV)	(A)	70	33	1·9 : 1
(IV)	(B)	78	20	5·7 : 1

[a] (A) = [(mesitylene)W(CO)$_3$], EtAlCl$_2$, and O$_2$; (B) = [Mo(NO)$_2$Cl$_2$(PPh$_3$)$_2$] and EtAlCl$_2$. [b] At low conversion after 20 min.

Two catalytic systems have been used, one based on a tungsten catalyst {[(mesitylene)W(CO)$_3$], EtAlCl$_2$, and O$_2$} and the other on a molybdenum catalyst {[Mo(NO)$_2$Cl$_2$(PPh$_3$)$_2$] and EtAlCl$_2$}, in chlorobenzene. The reactions were carried out at 25 °C in a batch reactor, and the reactants were introduced in the following order: olefin (2 mmol), W or Mo catalyst (0·1 mmol), EtAlCl$_2$ (2·4 mmol), and O$_2$ (for W) (8 mmol). The olefins (I)—(IV) were studied, and rates of conversion were followed by measuring the amount of ethylene [for (I), (II), or (III)] or but-2-ene [for (IV)] evolved (Table).

$CH_2{=}CHCH_2NH_2$ (I)
$CH_2{=}CHCH_2NMe_2$ (II)
$CH_2{=}CHCH_2NMe_3Br$ (III)
trans-$MeCH{=}CH[CH_2]_3NMe_3I$ (IV)

Whereas the olefins (I) and (II) do not undergo metathesis, those with a quaternary ammonium group do. With the olefin (IV), besides formation of but-2-enes, the diammonio-compound $(Me_3N[CH_2]_3CH{=}CH[CH_2]_3NMe_3)^{2+}2I^-$ was isolated (28% yield) and identified by n.m.r. spectroscopy: δ (D_2O; $Me_3SiCH_2CH_2CH_2SO_3Na$ internal reference) 2 (4 × CH_2), 3·1 (6 × Me), 3·5 (2 × CH_2), and 5·5 (CH=CH). Consequently, the overall stoicheiometry is characteristic of the metathesis reaction (1). In the case of this *trans* olefin,

$$2\,(Me_3CH{=}CH[CH_2]_3NMe_3)^+ \rightleftharpoons (Me_3N[CH_2]_3CH{=}CH[CH_2]_3NMe_3)^{2+} + MeCH{=}CHMe \qquad (1)$$

with a W-based catalyst, plots of conversion *vs*. time follow a sigmoid curve typical of an autocatalytic phenomenon, as usually occurs with *trans* olefins. Stereoselectivities were determined by the *trans* : *cis* ratio of the but-2-enes [metathesis of olefin (IV)] produced at low conversion. The values obtained (1·9 : 1 and 5·7 : 1 for, respectively, W-based or Mo-based catalysts) indicate that the *trans* isomer of the starting olefin gives predominantly *trans* isomers in the products, which is classical metathetic behaviour.[4] Metathesis of olefinic amines is thus possible by eliminating the basic character of the nitrogen.

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