

## Effect of Hydroperoxides on the Isomerization of Olefins Catalysed by a Ruthenium(II) Complex

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**Summary** The rate of olefin isomerization catalysed by  $\text{RuCl}_2(\text{Ph}_3\text{P})_3$  is greatly accelerated in the presence of small amounts of hydroperoxides which convert the ruthenium complex into a catalytically active compound having a CO ligand.

THE isomerization of olefins catalysed by group VIII metal complexes has received wide attention.<sup>1</sup> Much effort has been directed towards elucidation of the factors affecting isomerization of olefins during homogeneous hydrogenation in benzene-alcohol solutions.<sup>2-5</sup> Using a simpler system,  $\text{RuCl}_2(\text{Ph}_3\text{P})_3$  dissolved in olefinic hydrocarbons, we have examined the effect of two common contaminants, oxygen and hydroperoxides, on the homogeneous, catalytic isomerization of olefins in the absence of hydrogen.

110–113 °C, [40% of the weight of (I) used] having no i.r. absorption in the 2000  $\text{cm}^{-1}$  region, was recovered from the reaction mixture. The total yield of isomerization products using the purified olefin was less than 2% after 48 h at 100 °C.

More rapid rates of  $\text{Ru}^{\text{II}}$ -catalysed isomerization of the purified olefin could be observed if small amounts of either cumylhydroperoxide or *t*-butylhydroperoxide were introduced into the pure olefin prior to reaction. A tan solid having an i.r. spectrum and m.p. identical to those of complex (II) was isolated from each reaction mixture. Catalytic quantities of hydroperoxides *alone* did not isomerize pure 4-vinylcyclohexene at 100 °C. Complex (I) *alone* was nearly inactive toward isomerization of the pure olefin at this temperature. Complex (II), on the other

TABLE

Isomerization of olefins in the presence of  $\text{RuCl}_2(\text{Ph}_3\text{P})_3$ <sup>a</sup> and added substrates at 100 °C

Olefin	Added substrate	Substrate conc./mol l <sup>-1</sup>	Reaction time/h	% Isomerization <sup>b</sup>	Yield of CO-complex
4-Vinylcyclohexene	None		48	2	
"	c	c	48	99	60
"	<i>t</i> -Butylhydroperoxide	$6 \times 10^{-2}$	48	75	43
"	Cumylhydroperoxide	$6 \times 10^{-2}$	48	63	31
"	Oxygen	d	41	31	20
Allylbenzene	None		17	5	
"	<i>t</i> -Butylhydroperoxide	$6 \times 10^{-2}$	17	99	50 <sup>e</sup>
"	Oxygen	d	17	54	39 <sup>e</sup>

<sup>a</sup> A  $7 \times 10^{-3}\text{M}$  solution of  $\text{RuCl}_2(\text{Ph}_3\text{P})_3$  in the pure olefin stirred under nitrogen. <sup>b</sup> Products of isomerization of 4-vinylcyclohexene are mainly the 3- and 4-ethylidenecyclohexenes, and of allylbenzene are *cis*- and *trans*-propenylbenzene. <sup>c</sup> Olefin used was contaminated with hydroperoxides which had accumulated when set aside in air. <sup>d</sup>  $\text{O}_2$  bubbled vigorously through pure olefin for 2 min prior to reaction. <sup>e</sup> A tan solid m.p. 122–125°C (decomp.) having an intense i.r. band at 1980  $\text{cm}^{-1}$  (Nujol).

It has been reported that  $\text{RuCl}_2(\text{Ph}_3\text{P})_3$  (I) slowly isomerizes pent-1-ene in the absence of hydrogen or protic solvents.<sup>6</sup> We report that the  $\text{RuCl}_2(\text{Ph}_3\text{P})_3$ -catalysed isomerization of an olefin is greatly enhanced by introduction of small amounts of hydroperoxides and that the complex (I) is converted into a catalytically active *carbonyl* complex during the isomerization process.

A  $7 \times 10^{-3}\text{M}$  solution of (I) in 4-vinylcyclohexene which had not been freed of hydroperoxide impurities was warmed at 100 °C under nitrogen. After 48 h isomerization of the olefin was nearly complete. When the clear, orange solution had cooled, a new complex (II), m.p. 115–116 °C, was precipitated in 60% yield by addition of excess of pentane. Complex (II) was a tan solid which exhibited intense i.r. absorption at 1994 and 1092  $\text{cm}^{-1}$  characteristic of ruthenium-carbonyl<sup>7</sup> and co-ordinated triphenylphosphine respectively. Elemental analysis and molecular weight were consistent with the formula:  $\text{RuCl}_2(\text{CO})(\text{Ph}_3\text{P})_2(\text{C}_8\text{H}_{12})$ .

When, however, a similar isomerization was attempted using 4-vinylcyclohexene which was freed of reactive oxygen-containing impurities by percolating through activated silica gel prior to reaction, much of the ruthenium complex (I) did not dissolve in the diene, the rate of isomerization was greatly diminished, and a yellow solid, m.p.

hand was found to exhibit a high degree of isomerization activity in pure, hydroperoxide-free 4-vinylcyclohexene. Complete isomerization occurs in less than 48 h when (II) is used as the catalyst. It appears, therefore, that hydroperoxide reacts with (I) in the presence of 4-vinylcyclohexene to form the catalytically active complex (II). The addition of hydroperoxides to a variety of olefins including allylbenzene, vinylcyclohexane, vinylcyclopentane, allylcyclopentane, 1,7-octadiene, *etc.* caused greatly accelerated rates of  $\text{Ru}^{\text{II}}$ -catalysed isomerization and formed catalytically active carbonyl complexes which were isolated from the reaction mixtures.

Small amounts of oxygen were also found to be beneficial in the isomerization of pure olefins catalysed by complex (I). Rate enhancement was less pronounced than with hydroperoxides and lower yields of carbonyl complexes were isolated from these reaction mixtures. While we did not find significant quantities of ruthenium peroxo-complexes in the hydroperoxide-treated systems, solids exhibiting intense i.r. bands at 810–850  $\text{cm}^{-1}$ , characteristic of metal peroxo-complexes, were obtained from our isomerizations with added oxygen.

We also found that when small amounts of compounds which are easily decarbonylated by  $\text{Ru}^{\text{II}}$ ,<sup>8</sup> *i.e.*, benzyl formate, phenylacetaldehyde, *etc.* are added to olefin

solutions of (I), a large acceleration in the rate of isomerization occurs and complexes having a CO ligand are obtained. A similar effect was observed with added carbon monoxide; however results were complicated by rapid reaction to form

the dicarbonyl complex  $\text{RuCl}_2(\text{CO})_2(\text{Ph}_3\text{P})_2$ <sup>9</sup> which was insoluble in the reaction medium.

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