

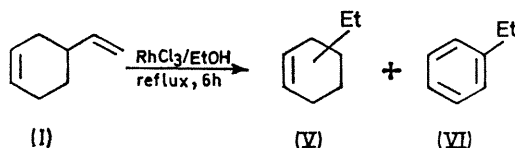
Sequential Rhodium-catalysed Isomerisation and Disproportionation of 4-Vinylcyclohexene

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Summary Quantitative conversion of 4-vinylcyclohexene into equimolar quantities of ethylbenzene and ethylcyclohexene occurs under the influence of catalytic quantities of rhodium trichloride in ethanolic solution

We report that rhodium trichloride in ethanolic solution catalyses the quantitative conversion of 4-vinylcyclohexene (I) into equimolar amounts of ethylbenzene (VI) and ethylcyclohexenes (V). The reaction, carried out at



reflux under nitrogen with catalyst concentrations in the range 0.02–0.05M occurs *via* a major intermediate, 4-ethylidenecyclohexene (II), and two minor ones, one of which is 1-ethylcyclohexa-1,4-diene (III) and the other has been tentatively identified as an isomer of ethylcyclohexa-1,3-diene (IV). The course of the reaction is shown by the results in the Table. The intermediate (II), the major

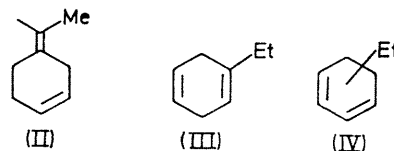
Catalysed isomerisation and disproportionation of 4-vinylcyclohexene

Time (h)	(I)	(II)	(III)	(IV)	(V)	(VI)
0	100	—	—	—	—	—
0.5	19	46	6	11	8	10
1	7	42	11	10	14	16
2	4	14	12	7	31	34
6	Trace	—	1	2	46	51

component after *ca* 1 h, was isolated by stopping the reaction at this stage and fractionating the mixture. The virtual disappearance of (II), (III), and (IV) from the

reaction mixture after 6 h indicates that they are *intermediates* in the formation of the final products. The ethylcyclohexenes consist of approximately equimolar mixture of the isomers 1-ethylcyclohexene and 3-ethylcyclohexene. Addition of pentane to the final product mixture gives a red-brown precipitate which has been identified as $(4\text{-vinylcyclohexeneRh}^{\text{I}}\text{Cl})_2$. No evidence of rhodium metal precipitation was observed.

Rhodium catalysts are known to promote 1,3-hydride shifts.¹ Lyons² has observed the disproportionation of cyclohexa-1,4-diene under the influence of iridium complexes of the type $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ (X = halogen) and Moseley and Matlis³ have reported that (cyclohexa-1,3-diene)(pentamethylcyclopentadienyl)rhodium(I) catalyses the analogous reaction with cyclohexa-1,3-diene. In consequence we believe that in the present work a sequence of two 1,3-hydride shifts occurs to give initially 4-ethylidenecyclohexene and then a mixture of ethylcyclohexadienes (III) and (IV), which in turn readily undergo disproportionation with the same catalyst to give ethylcyclohexene and ethylbenzene.



Attempts to promote this reaction with rhodium(I) complexes, *e.g.* $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhCl}(\text{PPh}_3)_3$ under similar conditions gave negligible product formation. Thus, fairly ready isomerisation and disproportionation occur when an *in situ* rhodium(I) catalyst, *i.e.* $\text{RhCl}_3/\text{EtOH}$,¹ is used and sophisticated ligands may be impediments rather than assets.

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¹ R Cramer *Accounts Chem Res*, 1968 **1** 186

² J E Lyons *Chem Comm*, 1969, 564

³ K Moseley and P M Matlis *Chem Comm*, 1969 1156