# The Disproportionation of Cyclohexa-1,3-diene to Benzene and Cyclohexene Catalysed by (Cyclohexa-1,3-diene)(pentamethylcyclopentadienyl)rhodium

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*Summary* (Cyclohexa-1,3-diene)(pentamethylcyclopentadienyl)rhodium, (IIa), is a very active catalyst for disproportionation of cyclohexa-1,3-diene to cyclohexene and benzene, and cyclohexa-1,4,-diene is isomerised to the 1,3-isomer during the formation of the complexes (II).

WE have found that (cyclohexa-1,3-diene)(pentamethylcyclopentadienyl)rhodium, (IIa) is an active catalyst for the disproportionation of cyclohexa-1,3-diene. This contrasts with the observation of Lyons who recently found that the 1,4-diene, but *not* the 1,3-, was similarly disproportionated by some iridium catalysts.[1] The 1,4-diene was also disproportionated to some extent in our reactions, but this appeared to proceed *via* primary isomerisation of the 1,4- to the 1,3-isomer here. The iridium complex (IIb) was inactive for both reactions.

The complexes (II) were obtained† from the pentamethylcyclopentadienylmetal dichlorides (I)[2,3] and either cyclohexa-1,3- or -1,4-diene (EtOH–$Na_2CO_3$/35—50°).

The formation of the complexes (II) from the 1,4-diene

*Isomerisation and disproportionation of cyclohexadienes catalysed by* $C_5Me_5Rh(C_6H_8)$ (IIa).[a]

| | | (IIa) recovered | Cyclohexene | Benzene | Cyclohexadiene | |
|---|---|---|---|---|---|---|
| Diene | Conditions | % | % | % | 1,3 % | 1,4 % |
| Cyclohexa-1,3-diene | $Na_2CO_3$–EtOH/55°/5 hr. | 85 | 41 | 48 | trace | 0 |
| | EtOH/55°/4 hr. | 85 | 15 | 17 | 75 | 0 |
| | n-Hexane/66°/6·5 hr. | 100 | 0 | 0 | 100 | 0 |
| | THF/65°/21 hr. | 95 | 6 | 6 | 86 | 0 |
| Cyclohexa-1,4-diene | $Na_2CO_3$–EtOH/60°/4 hr. | 85 | 5 | 6 | 11 | 63 |
| None | $Na_2CO_3$–EtOH/60°/3 hr.[b] | 78 | 4 | 5 | 0 | 0 |

[a] Reactions were carried out using freshly sublimed samples of (IIa) and purified dienes, under nitrogen. The volatile products were analysed by g.l.c. on two different columns. No cyclohexane was ever detected.

[b] No free metal was ever formed, even in the absence of diene.

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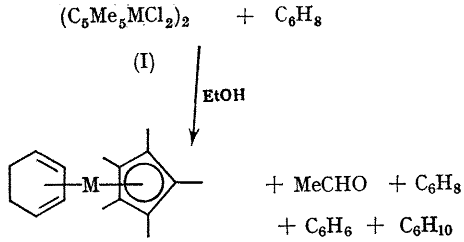
† As bright yellow crystals, completely characterised by analyses and spectroscopically.

was accompanied by isomerisation of uncomplexed 1,4- to 1,3-diene (Rh, 4; Ir, 33%) and by disproportionation (Rh, 25; Ir, 6%). More detailed studies of these reactions indicated that isomerisation was probably the precursor to disproportionation.



(II)

a; M=Rh
b; M=Ir

The formation of (II) from the 1,3-diene was accompanied by disproportionation only (Rh, 95; Ir, <9%). For both sets of reactions the degree of disproportionation depended on the length of time and the temperature of reaction.

We concluded the isomerisation (1,4- to 1,3-) largely occurred concurrently with the formation of (II) (however, see Table), but that (IIa) itself was the most active catalyst for the disproportionation.

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