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OLEFIN ISOMERISATIONS USING TRISTRIPHENYLPHOSPHINERHODIUM CHLORIDE

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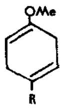
Tristriphenylphosphinerhodium chloride has been used as an oxidation[1] and an hydrogenation[2] catalyst and in only one case[3] has double-bond isomerisation been noted. A number of other transition metal complexes are known to produce double-bond isomerisation, e.g.,[4] although this is frequently accompanied by complex formation. We have now observed that the rhodium complex acts cleanly as a catalyst for the conjugation of 1,4-dienes to 1,3-dienes. The procedure is a mild one, in contrast to previous methods involving strong bases such as potassamide in liquid ammonia[5] or potassium tert-butoxide in dimethylsulphoxide.[6]

1-Methoxycyclohexa-1,4-diene (I,R=H) was equilibrated[5] with the more stable conjugated isomer 1-methoxycyclohexa-1,3-diene (II,R=H)(80%) by refluxing in chloroform for 2 hours with the catalyst (1% by weight). No reaction was observed at room temperature; benzene was also found to be a useful solvent, the isomerisation being somewhat slower. Similarly (I,R=Me) was equilibrated with (II,R=Me).

Base-catalysed isomerisations of 3-alkyl-1-methoxycyclohexa-1,4-dienes give first the endocyclic conjugated diene[7] and then the more stable exocyclic diene, e.g. (III,R=H) ⟶ (IV,R=H) ⟶ (V,R=H). The present conditions produce the same final product in this and other cases, e.g. (VI)⟶(VII) and (IX)⟶(X), without so far permitting the reaction to be arrested at the intermediate cis-diene (e.g. VIII). Using benzene as a solvent, it was possible to obtain a small proportion of (VIII) from (VI) with mainly (VII) but in refluxing chloroform after 5 minutes (VII) was the only product. For reasons already defined[7] the base-catalysed conjugation of (III,R=Me) is arrested at (IV), but with the rhodium catalyst the product (V,R=Me) is obtained. This was identified by hydrolysis to the ketone (XI) the spectra of which accord with the structure given, notably ν_{max} 1710 cm^{-1}, τ 8.56s(3H), 8.60s(3H) and the absence of resonances in the olefinic region.

Safrole (XII), in chloroform, gave a mixture of cis-isosafrole (40%) and trans-isosafrole (60%). Using benzene for the same period of reflux (2 hours) the only product was cis-isosafrole (60%) and unchanged safrole, but after 3 hours some trans-isosafrole (20%) had appeared. The initial product therefore seems to be entirely cis, which is slowly converted into the trans-isomer.

In all cases except (XI) and (V,R=Me) the products are known and were compared with authentic ones by g.l.c., and by p.m.r. spectra, and in the case of (X) by mixed m.p. 110-112°.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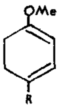
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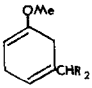
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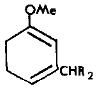
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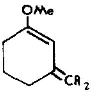
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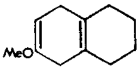
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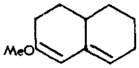
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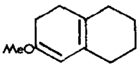
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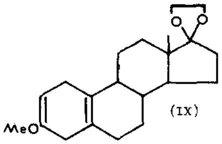
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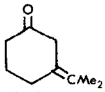
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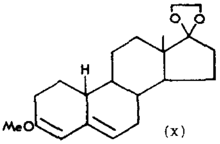
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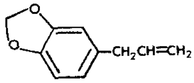
(XII)

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