The Mechanism of the Reaction of Phenylmanganese Carbonyl with Buta-1,3-diene

By M. GREEN and R. I. HANCOCK

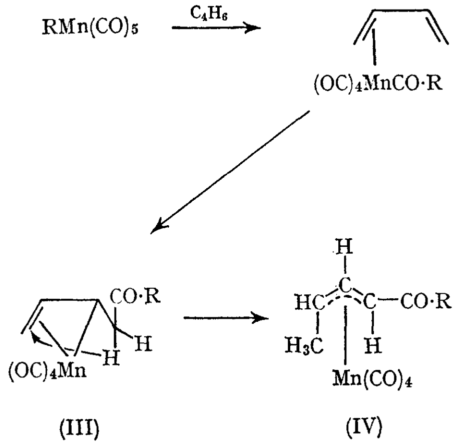
(*Department of Inorganic Chemistry, The University, Bristol*, 8)

THE π-allylic complexes (Ia or b) are obtained by treating buta-1,3-diene with methyl- or phenylmanganese carbonyl respectively.[1] This reaction is particularly interesting because in the formation of the skeletal arrangement (MeCH·CH·CH·CO·R) from buta-1,3-diene it appears that a 1,4-hydrogen shift occurs.

There are now a number of examples of a hydrogen atom in a hydrocarbon ligand migrating in the presence of a transition metal;[2] however, few mechanistic studies have been previously reported. We describe deuterium-labelling experiments which lead to a more detailed understanding of the reaction of $RMn(CO)_5$ (R=Me or Ph), with buta-1,3-diene.

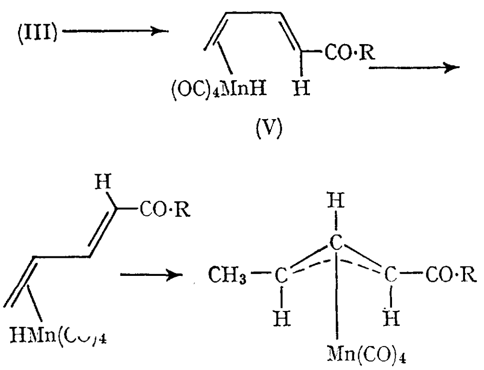
Phenylmanganese carbonyl reacted smoothly with $[1,1,4,4\text{-}^2H_4]$buta-1,3-diene[3] affording a deuterated π-allylic complex. The ^1H n.m.r. spectrum of the complex measured in $CDCl_3$ at 100 Mc./sec. showed three groups of bands at τ 2·33 (complex, aromatic hydrogens), 4·17 (doublet, J_{HH} = 12 c./sec) and 6·44 (doublet, J_{HH} = 12 c./sec.) with relative integrated intensities of 5 : 1 : 1 respectively. The coupling of 12 c./sec. is typical of that observed between *trans*-hydrogens in π-allylic complexes, and comparison of the spectrum of the deuterated complex with that of the non-deuterated complex (Ib) showed that the observed doublets can be assigned to hydrogens 2 and 3 in (Ib). This was supported by the fact that double irradiation of either of the two doublets resulted in a collapse of the other doublet to a sharp singlet, and by the absence of bands with chemical shifts corresponding to the hydrogens $C\mathit{H}_3$·CH·CH·CH·CO·Ph or CH_3·CH·CH·*CH*·CO·Ph in (Ib). These observations clearly show that the deuterated π-allylic complex has the structure (II), that is a 1,4-hydrogen shift has occurred, and therefore mechanisms in which a hydrogen moves from one carbon to the next can be excluded.

Any mechanism which explains the observed 1,4-hydrogen shift must also explain the stereochemistry of the π-allylic complexes (Ia or b), and therefore the attractive mechanism depicted in Scheme 1 may be discounted, since it is unlikely that the complex (IV) would isomerise to (Ib) at room temperature.

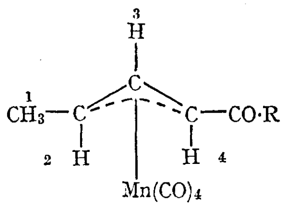


SCHEME 1

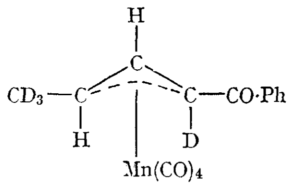
It is suggested that the reaction path actually followed is that shown in Scheme 2. As in Scheme 1 it is assumed that the diene co-ordinates on to the manganese with the displaced CO inserting into the carbon–manganese bond. This is followed by a 1,2-addition of $RCOMn(CO)_4$ to the unco-ordinated double bond of the diene in a cisoid conformation. The bulky acyl group in intermediate (III) would then be expected to adopt the more stable transoid conformation. The elimination of $HMn(CO)_4$ from (III) affords (V), which would be free to adopt the transoid conformation. Then addition of $HMn(CO)_4$ to the terminal methylene group leads to a π-allylic complex with the correct stereochemistry.



SCHEME 2



(I) a; R=Me
b; R=Ph



(II)

(*Received, July 14th,* 1966; *Com.* 500.)

---

[1] W. D. Bannister, M. Green, and R. N. Haszeldine, *J. Chem. Soc. (A)*, 1966, 194.

[2] N. R. Davies, *Austral. J. Chem.*, 1964, **17**, 212; E. S. Stern, *Proc. Chem. Soc.*, 1963, 111; R. E. Rinehart and J. S. Lasky, *J. Amer. Chem. Soc.*, 1964, **86**, 2516; J. E. Arnet and R. Pettit, *ibid.*, 1961, **83**, 2954; J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843; R. Cramer, *J. Amer. Chem. Soc.*, 1966, **88**, 2272.

[3] A. C. Cope, G. A. Berchtold, and D. L. Ross, *J. Amer. Chem. Soc.*, 1961, **83**, 3859.