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THE STEREOCHEMISTRY OF CLEAVAGE OF SOME ALKENYLMANGANESE CARBONYL DERIVATIVES

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SUMMARY

Cleavage of the compounds *trans*-$RCH{=}CR{-}Mn(CO)_5$ (where $R = CF_3$, CO_2Me or CO_2H) with $HMn(CO)_5$ occurs with complete retention of configuration to yield the corresponding *trans*-olefins and $Mn_2(CO)_{10}$. Reaction of the compound where $R = CF_3$ with bromine occurs similarly with retention of configuration to give *trans*-$CF_3CH{=}C(CF_3)Br$, whereas cleavage of the compound where $R = CO_2H$ with bromine proceeds with complete inversion of configuration. The compounds *cis*-$MeO_2CCH{=}CH{-}Mn(CO)_5$ and *trans*-$MeO_2CCH{=}C(CO_2Me){-}Mn(CO)_5$ react with bromine to give mixtures of *cis*- and *trans*-$MeO_2CCH{=}CHBr$ (ratio *cis/trans* 3/7), and *cis*- and *trans*-$MeO_2CCH{=}CBr{-}CO_2Me$ (ratio *cis/trans* 7/3) respectively.

Hydridopentacarbonylmanganese has also been shown to react with MeC_2Me or EtC_2Et to give mainly *cis*-2-butene and *cis*-3-hexene respectively, probably by a *cis* hydride addition followed by stereospecific hydride cleavage. Diphenylacetylene under similar conditions gives *trans*-stilbene, but as rapid *cis/trans* isomerisation has also been shown to occur under these conditions, no conclusions regarding the stereochemistry of the hydride addition step could be reached.

INTRODUCTION

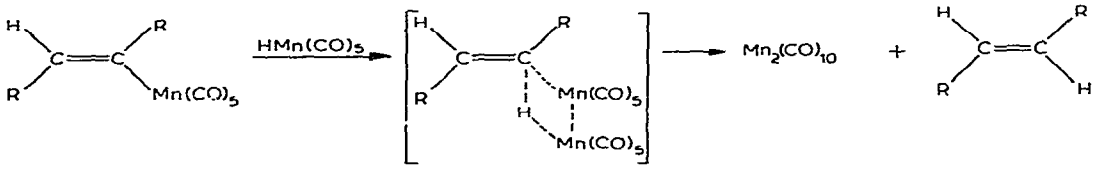
Cleavage of alkyl–manganese bonds is well known[1] to occur with acids and halogens, but little is known about the mechanisms of these reactions. Recent work by Pearson[2] has shown that cleavage of an optically active alkylpentacarbonylmanganese complex with bromine occurs with retention of configuration. The acid cleavage of the compounds $CF_3CH{=}C(CF_3){-}Mn(CO)_5$[3], and $CH_3CO{-}CH{=}C(CO_2Me){-}Mn(CO)_4$[4] has also been shown to occur with retention of stereochemistry. We now report some observations on the stereochemistry of cleavage of some alkenyl–manganese carbonyl compounds with hydridopentacarbonylmanganese and bromine.

RESULTS AND DISCUSSION

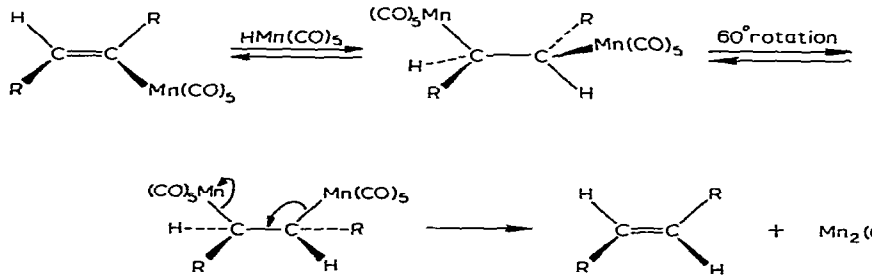
Cleavage reactions with $HMn(CO)_5$

Reaction of the compounds *trans*-$RO_2CCH{=}C(CO_2R){-}Mn(CO)_5$ (where

R=H or Me)[5] with hydridopentacarbonylmanganese at room temperature over several days gave decacarbonyldimanganese and fumaric acid (45%) and dimethyl fumarate (91%) respectively; no trace of the corresponding maleate derivatives could be detected among the reaction products. Thus cleavage of the carbon–manganese bond with the hydride occurs with retention of configuration. Further support for this conclusion came from a re-investigation of the reaction of $HMn(CO)_5$ with hexafluoro-2-butyne. This reaction has been reported previously[3] to give a 13% yield of the 1/1 adduct *trans*-$CF_3CH{=}C(CF_3){-}Mn(CO)_5$. We have confirmed these findings, but examination of the volatile reaction products has also shown that the major product is *trans*-$CF_3CH{=}CHCF_3$ formed in 88% yield. A trace (1%) of *cis*-$CF_3CH{=}CHCF_3$ was also obtained from this reaction. This could indicate that some *cis*-$CF_3CH{=}C(CF_3){-}Mn(CO)_5$ may be formed as a minor product of the initial hydride addition, but attempts to detect the *cis*-adduct were unsuccessful. It seems very probable that a similar stereospecific hydride cleavage also occurs in the reaction of $HCo(CO)_4$ with $CF_3C_2CF_3$ which is reported[6] to yield *trans*-$CF_3CH{=}CHCF_3$ exclusively. These hydride cleavage reactions may proceed by one of several possible mechanisms. The most plausible of these seem to be either a mechanism involving a four-centre cyclic transition state:



or an addition/elimination type mechanism.



The alternative of a *cis*-addition followed by a *trans*-elimination seems rather rather less probable in view of the preference shown for *trans*-addition by metal carbonyl hydrides on reaction with electron-defficient unsaturated compounds.

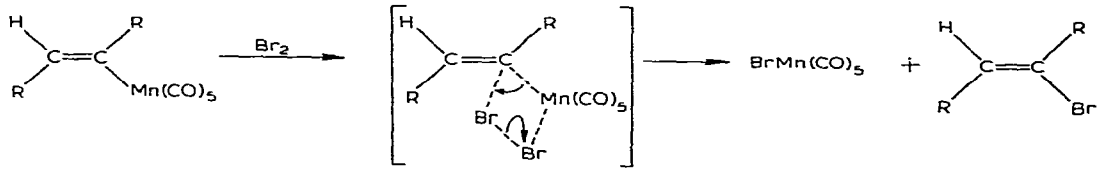
Cleavage reactions with bromine

Reaction of *trans*-$CF_3CH{=}C(CF_3){-}Mn(CO)_5$ with bromine at room temperature over 14 days gave bromopentacarbonylmanganese (65%) and a product thought to be $CF_3CH{=}CBr{-}CF_3$. Its ^1H NMR spectrum showed a quartet at 0.38 ppm to low field of benzene due to the vinylic proton [J(H–F) 7 Hz], and the ^{19}F NMR spectrum showed two signals of equal intensity at 16.53 [doublet, J(H–F)

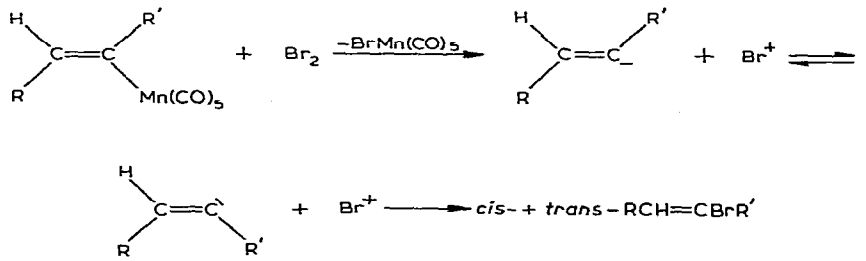
7 Hz] and 9.60 ppm (singlet) to low field of trifluoroacetic acid due to CF_3 groups in different environments; the signal at 9.60 ppm being assigned to the CF_3 adjacent to the bromine atom, and that at 16.53 ppm is assigned to the CF_3 adjacent to the vinylic proton. The absence of $^{19}F-^{19}F$ coupling establishes[7] a relative *trans*-configuration for the two CF_3 groups. Thus this bromine cleavage reaction proceeds with retention of the stereochemistry about the double bond.

The reaction of bromine with *trans*-$HO_2CCH=C(CO_2H)-Mn(CO)_5$ gave an almost quantitative yield of bromomaleic acid, identified by mixed m.p., IR and ^1H NMR spectroscopy. The similar reaction of *trans*-$MeO_2CCH=C(CO_2Me)-Mn(CO)_5$ gave a 92% yield of a mixture shown by ^1H NMR spectroscopy to consist of dimethyl bromomaleate and dimethyl bromofumarate in the ratio of 7/3. Bromine cleavage of the compound *cis*-$MeO_2CCH=CH-Mn(CO)_5$, obtained from the reaction of methyl propiolate with $HMn(CO)_5$[5], similarly gave a mixture of *trans*- and methyl *cis*-3-bromoacrylate in the ratio of 7/3. The products from these reactions were all identified by comparison of their ^1H NMR spectra with those of authentic samples synthesised by previously reported routes. Thus, in contrast to the reaction of $CF_3-CH=C(CF_3)-Mn(CO)_5$ with bromine these reactions proceed either exclusively or predominantly with inversion.

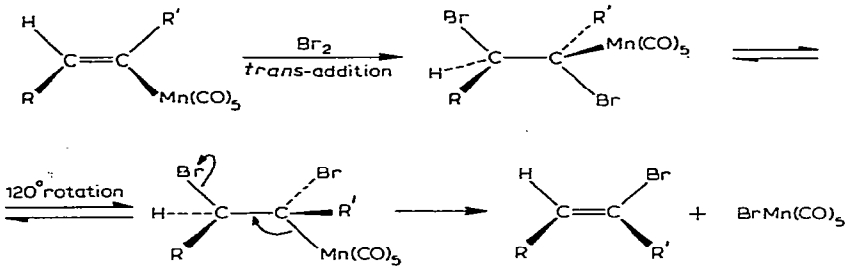
In the case where the stereochemistry about the double bond is retained attack of bromine possibly occurs initially at the manganese atom, followed by attack at carbon via a four centre transition state, not necessarily synchronous, to give the isolated products.



In some respects this mechanism is similar to that postulated for certain cleavage reactions of organomercurials[8,9]. For a similar mechanism to operate in the reactions which proceed with inversion it seems necessary to postulate that the carbon–manganese bond breaks before attack by bromine occurs, *i.e.* an S_E1 mechanism. The resultant carbanion could then undergo inversion leading to mixed



products. On this basis, however, it is difficult to appreciate why inversion about the double bond is preferred. Perhaps a more plausible explanation is that these reactions which take place with inversion involve initial attack by bromine at the olefinic bond rather than at the manganese atom. The intermediate thus formed could then undergo



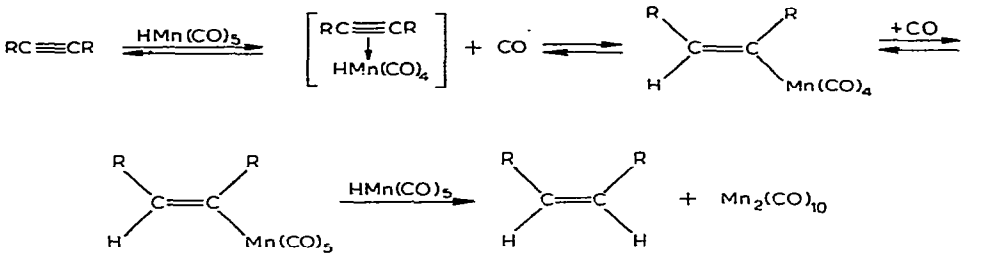
a *trans*-β-elimination reaction to give the isolated products.

The bromofumarate and *cis*-3-bromoacrylate derivatives also isolated from the reactions with *trans*-$MeO_2CCH{=}C(CO_2Me){-}Mn(CO)_5$ and *cis*-$MeO_2CCH{=}CH{-}Mn(CO)_5$ respectively, may arise by a competing four-centre reaction as discussed previously for the reaction of $CF_3CH{=}C(CF_3){-}Mn(CO)_5$.

Reactions of hydridopentacarbonylmanganese with some alkyl- and aryl-substituted acetylenes

Our interest[5] in the stereochemistry of hydride addition to acetylenes led us to investigate the reactions of $HMn(CO)_5$ with 2-butyne, 3-hexyne and diphenylacetylene. Previous work has shown that metal carbonyl hydrides normally undergo *trans*-addition reactions with acetylenes substituted by electron-withdrawing groups[3,5,10,11]. Although variation in the nature of the ligands on the metal atom can lead to *cis*-addition[5,12]. It was of interest, therefore, to examine how changes in the nature of the acetylene affected the stereochemistry of hydride addition.

Hydridopentacarbonylmanganese did not react with 2-butyne at room temperature over a period of several days, but at 80° a slow reaction occurred to give *cis*-2-butene (43%) and *trans*-2-butene (5%). The similar reaction of 3-hexyne at 100° for 10 days gave a 75% yield of *cis*-3-hexene, together with some *trans*-3-hexene (9%), *cis*-2-hexene (11%) and *trans*-2-hexene (5%). The formation of low yields of *cis*- and *trans*-2-hexene in this reaction is considered to arise by a hydride-catalysed double bond isomerisation reaction; a reaction which is well known to occur with other metal carbonyl hydrides[13]. It is reasonable to assume that the formation of olefins in these reactions proceeds by an initial hydride addition to give an unstable alkenylmanganese carbonyl intermediate, which then undergoes rapid hydride cleavage to give the isolated products. If it is assumed, on the basis of the experiments described earlier, that the hydride cleavage step occurs with retention of configuration, then the isolation of *cis*-olefins as the major products from these reactions clearly indicates that the initial hydride addition to the acetylenes is also *cis*. This is in marked contrast to the *trans*-addition observed with the acetylenes RC_2R' (where $R{=}R'{=}CF_3$, CO_2H or CO_2Me; $R{=}H$, $R'{=}CO_2Me$). It is probable that the reactions of $HMn(CO)_5$ with electron-rich acetylenes occur by rearrangement of a π-complex via a four centre cyclic transition state. Although the formation of low yields of *trans*-2-butene and *trans*-3-hexene in these reactions could indicate that some *trans*-adduct is also formed during these reactions, an alternative explanation is that these products arise by isomerisation of the *cis*-olefin. In support of this latter proposal it has been shown that when a mixture of *cis*- and *trans*-2-hexene (*cis*/*trans* 55/41) was heated with $HMn(CO)_5$ under similar conditions to those employed for



he reaction of 3-hexyne, analysis of the olefin mixture at the end of the reaction howed a ratio of *cis/trans*-2-hexene of 33/42, indicating that some *cis/trans* isomerisation had occurred during the reaction. This result is open to some doubt as n-hexane 5%) and *trans*-3-hexene (12%) were also identified among the reaction products. Iowever, it seems unlikely that these products arise solely from *cis*-2-hexene, as vould be necessary to account for the observed decrease in the amount of the *cis*-somer. Although the similar reaction of *cis*-3-hexene was not investigated, it seems ery probable that isomerisation of this compound would also occur under similar onditions. The *cis/trans* isomerisation reaction could take place by a hydride ddition/elimination reaction in which both steps occur in a *cis* manner, as recently roposed for the similar reaction with $HCo(CO)_4$[14].

The reaction of $HMn(CO)_5$ with diphenylacetylene gave inconsistent results. On one occasion when this reaction was carried out at room temperature a rapid, xothermic reaction occurred over ca. 10 min to give a 27% yield of *trans*-stilbene nd a low yield of a solid identified by analysis, IR and ^1H NMR spectroscopy as *rans*-2,3-diphenylacrolein. Several subsequent attempts to repeat this reaction were nsuccessful. On these occasions no reaction occurred over 7 days at room temperature either in the absence of solvent or in diethyl ether. When the reaction was arried out in tetrahydrofuran (THF) at room temperature over 7 days a 19% yield f *trans*-stilbene was obtained, but no acrolein derivative could be detected. The act that this reaction could not be reproduced led us to the conclusion that the eaction to form *trans*-2,3-diphenylacrolein was possibly catalysed by some impurity n the hydride which was not present in samples used in subsequent experiments. Iowever, attempts to identify this impurity were unsuccessful.

When the reaction of $HMn(CO)_5$ and diphenylacetylene was carried out at igher temperatures the reaction products were decacarbonyldimanganese, *trans*-

TABLE 1

EACTIONS OF $HMn(CO)_5$ WITH DIPHENYLACETYLENE

$HMn(CO)_5$ mmole)	PhC_2Ph (mmole)	Solvent	Temp. (°C)	Time (days)	*trans*-PhCH=CHPh (%)	$(PhCH_2-)_2$ (%)
5.0	5.0		25	7		
5.0	5.0	Et_2O	25	7		
5.1	5.0	THF	25	7	19	
10.0	5.0		80	7	50	20
10.0	5.0	THF	80	7	48	26

stilbene and bibenzyl (see Table 1). The formation of *trans*-stilbene in these reactions is in contrast to the *cis*-olefins isolated as the major products from the reactions of 2-butyne and 3-hexyne. However, in a separate experiment it was shown that the reaction of $HMn(CO)_5$ and *cis*-stilbene at 100° for 2 days gave *trans*-stilbene and bibenzyl; no *cis* stilbene could be detected in the reaction mixture. When this reaction was repeated at room temperature over 4 weeks 61% of the *cis*-stilbene was recovered together with a 17% yield of *trans*-stilbene and 6% of bibenzyl. It is apparent from these results that the formation of *trans*-stilbene from the reaction of diphenylacetylene could arise either directly or by isomerisation of the initially formed *cis*-isomer, and further work is necessary to differentiate between these two possibilities.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 21 spectrometer, and NMR spectra were recorded on a Perkin–Elmer R 10 instrument operating at 56.46 MHz for ^{19}F and 60.0 MHz for ^{1}H. GLC analyses were carried out on a Perkin–Elmer 154c Fraktometer with 4 m columns packed with silver nitrate/ethylene glycol (30% by weight) on Celite.

Hydridopentacarbonylmanganese was prepared from (methylcyclopentadienyl)tricarbonylmanganese by an adaptation of the procedure reported for the preparation of decacarbonyldimanganese[15]. Dimethyl (pentacarbonylmanganese)-fumarate, (pentacarbonylmanganese)fumaric acid, and methyl *cis*-3-(pentacarbonylmanganese)acrylate were prepared as reported previously[5]. Bromomaleic acid, m.p. 136° (reported[16] 136–138°), was prepared from fumaric acid by bromination to give *meso*-α,β-dibromosuccinic acid (67%)[17], followed by reaction with P_4O_{10} to give bromomaleic anhydride (68%)[16] and finally hydrolysis of the anhydride to give the acid in 91% yield. The ^{1}H NMR spectrum of bromomaleic acid in acetone had bands at τ 3.37 (singlet) and τ −0.41 (singlet), in the intensity ratio of 1/2. Bromofumaric acid, m.p. 185–186° (reported[18] 185–186°) was prepared in 84% yield by reaction of hydrobromic acid with acetylene dicarboxylic acid; its ^{1}H NMR spectrum (acetone) showed bands at τ 2.41 (singlet) and τ 0.65 (singlet) in the ratio of 1/2. Dimethyl bromomaleate, b.p. 88–90°/8 mm, (Found: C, 32.6; H, 3.2. $BrC_6H_7O_4$ calcd.: C, 32.3; H, 3.1%.) and dimethyl bromofumarate, m.p. 28–29° (reported[19] 30°), were obtained in 26 and 44% yields respectively by esterification of the corresponding acids[20]. The ^{1}H NMR spectrum of the maleate (in CCl_4) showed bands at τ 3.58 (singlet), 6.17 (singlet) and 6.28 (singlet) in the intensity ratio of 1/3/3. Methyl *trans*-3-bromoacrylate, b.p. 85–87°/80 mm (Found: C, 29.1; H, 3.0. $BrC_4H_5O_2$ calcd.: C, 29.0; H, 3.1%.), was obtained in 71% yield by esterification of the corresponding acid at room temperature for 4 days. The acid, m.p. 113° (reported[20] 115–116°) was obtained in 45% yield from the reaction of propiolic acid with aqueous hydrobromic acid[20]. The ^{1}H NMR spectrum (CCl_4) of the acrylate showed an AB pattern centred at τ 2.95 (J_{AB} 14 Hz) and a singlet at τ 6.28 in the ratio of 2/3.

Cleavage reactions with hydridopentacarbonylmanganese

(a). Dimethyl (pentacarbonylmanganese) fumarate. A solution of hydridopentacarbonylmanganese (0.58 g, 2.96 mmole) and dimethyl (pentacarbonylmanganese)-fumarate (1.0 g, 2.9 mmole) in pentane (10 ml) was kept at room temperature for

1 week in a tube sealed under vacuum, whereupon a mixture of white and yellow crystals separated. Removal of the solvent, and sublimation of the solid residue *in vacuo* at 25° gave white crystals of dimethyl fumarate (0.39 g, 2.71 mmole, 91%), m.p. 100–101° (reported[21] 102°), which had an IR spectrum identical to that of an authentic sample. The orange, crystalline, sublimation residue was shown to be decacarbonyldimanganese (1.0 g, 2.55 mmole, 86%) by IR spectroscopy.

(*b*). *(Pentacarbonylmanganese)fumaric acid.* A solution of hydridopentacarbonylmanganese (0.75 g, 3.82 mmole) and (pentacarbonylmanganese)fumaric acid (1.2 g, 3.87 mmole) in diethyl ether (10 ml) was shaken in a tube at room temperature for 5 days. On opening the tube carbon monoxide (112 ml) was obtained indicating that some decomposition had occurred during the reaction. Removal of the ether, and extraction of the solid residue with aqueous acetone (3 × 10 ml), followed by evaporation of the aqueous acetone from the extract, gave a brown solid. Extraction of this solid with water (3 × 5 ml) and evaporation of the water from the extract under reduced pressure gave fumaric acid (0.20 g, 1.72 mmole, 45%), m.p. 284° (sealed tube; reported[21] 286–287°); the IR spectrum of the acid was identical to that of an authentic sample.

The residue from the aqueous acetone extraction was dried and extracted with light petroleum (b.p. 40–60°) to give decacarbonyldimanganese (0.82 g, 2.09 mmole, 54%), and a petrol-insoluble residue (0.4 g) which showed the presence of carboxyl groups and terminal metal carbonyl groups in its IR spectrum.

Cleavage reactions with bromine

(*a*). *trans-1,1,1,4,4,4-Hexafluoro-2-(pentacarbonylmanganese)-2-butene.* The fluoroalkene derivative (0.80 g, 2.23 mmole) and a solution of bromine (0.35 g, 2.23 mmole) in carbon tetrachloride (3 ml) were kept at room temperature for 14 days in a tube sealed under vacuum. The volatile products were transferred *in vacuo* to an external trap, shaken with mercury (15 ml) to remove any excess bromine, and the resulting colourless solution was examined by IR and NMR spectroscopy. The IR spectrum showed bands at 3040 w (C–H), 1664 w (C=C) and strong bands in the region of 1300–1000 cm^{-1} (C–F). The ^{19}F NMR spectrum showed a doublet at 16.52 [J(H–F) 7 Hz] and a singlet at 9.60 ppm to low field of external trifluoroacetic acid; the ^1H NMR spectrum (external benzene) showed a quartet at 0.38 ppm [J(H–F) 7 Hz] to low field of benzene, in good agreement with the spectra expected for *trans*-2-bromo-1,1,1,4,4,4-hexafluoro-2-butene[7].

The orange, crystalline residue (0.70 g) in the reaction tube was sublimed at room temperature under vacuum to yield recovered starting material (0.30 g, 0.84 mmole, 38%), and a sublimation residue identified as bromopentacarbonylmanganese (0.40 g, 1.45 mmole, 65%) by IR spectroscopy.

(*b*). *(Pentacarbonylmanganese)fumaric acid.* An excess of bromine (5 ml) was added under an atmosphere of nitrogen to (pentacarbonylmanganese)fumaric acid (1.10 g, 3.23 mmole) in a flask at 0°, and the reactants were shaken for 10 min at this temperature and then kept at room temperature for a further 20 min. Removal of the excess of bromine gave an orange solid (1.5 g), which on extraction with water (3 × 2 ml), and evaporation of the aqueous extract yielded yellow crystals of bromomaleic acid (0.6 g, 3.08 mmole, 97%) with identical mixed m.p., IR and ^1H NMR spectra to those of an authentic sample; no bromofumaric acid could be detected.

The extraction residue was bromopentacarbonylmanganese (0.85 g, 3.1 mmole, 96%).

(*c*). *Dimethyl (pentacarbonylmanganese)fumarate.* Dimethyl (pentacarbonylmanganese)fumarate (1.40 g, 4.14 mmole) and a solution of bromine (0.67 g, 4.19 mmole) in carbon tetrachloride (5 ml) were kept at room temperature for 14 days in in a tube sealed under vacuum. The solution was then filtered to give bromopentacarbonylmanganese (1.0 g, 3.64 mmole, 88%), and the filtrate was shaken with mercury (2 ml). After filtration to remove mercuric bromide and any excess mercury, the carbon tetrachloride was removed from the filtrate to yield a pale yellow oil (0.85 g, 3.81 mmole, 92%), which was shown by IR and ^{1}H NMR spectroscopy to be a mixture of dimethyl bromofumarate and dimethyl bromomaleate in the ratio of 3/7 by comparison with authentic samples of these compounds.

(*d*). *Methyl cis-3-(pentacarbonylmanganese)acrylate.* A solution of bromine (1.1 g, 6.88 mmole) in carbon tetrachloride (10 ml) was added dropwise over 10 min with occasional shaking to a solution of methyl *cis*-3-(pentacarbonylmanganese)-acrylate (1.80 g, 6.43 mmole) in carbon tetrachloride (20 ml) cooled at 0°, and the mixture was kept at this temperature for a further 15 min. Bromopentacarbonylmanganese (1.3 g, 4.73 mmole, 69%) was filtered off, and the filtrate was shaken with mercury (2 ml). Filtration, and evaporation of the solvent from the filtrate gave a colourless oil (1.02 g, 6.20 mmole, 96%) whose ^{1}H NMR spectrum in carbon tetrachloride showed an AB pattern centred at τ 2.95 (J_{AB} 14 Hz, *trans* vinylic protons), an AB pattern centred at τ 3.21 (J_{AB} 8 Hz, *cis* vinylic protons), and a singlet at τ 6.28 in the intensity ratio of 7/3/15, indicating that the oil was a 70/30 mixture of *trans*- and *cis*-3-bromoacrylate.

Reactions of hydridopentacarbonylmanganese with acetylenes

(*a*). *Hexafluoro-2-butyne.* When hydridopentacarbonylmanganese (5.0 g, 25,5 mmole) and hexafluoro-2-butyne (4.8 g, 29.6 mmole) were mixed in a tube at room temperature a vigorous, exothermic reaction occurred over ca. 5 min. Analysis of the volatile reaction products (4.3 g) by IR, ^{1}H NMR and ^{19}F NMR spectroscopy showed the presence of recovered hexafluoro-2-butyne (2.58 g, 15.9 mmole, 54%), *trans*-1,1,1,4,4,4-hexafluoro-2-butene (1.68 g, 10.4 mmole, 35%), and *cis*-1,1,1,4,4,4-hexafluoro-2-butene (0.04 g, 0.02 mmole, 1%) by comparison with the spectra of authentic samples. The oily residue (5.4 g) was sublimed at room temperature *in vacuo* to give *trans*-1,1,1,4,4,4-hexafluoro-2-(pentacarbonylmanganese)-2-butene (1.1 g, 3.1 mmole, 10%) as a pale yellow liquid, identified by comparison of its IR, ^{1}H NMR and ^{19}F NMR spectra with those previously reported[3]. Recrystallisation of the sublimation residue from light petroleum at −20° gave decacarbonyldimanganese (4.0 g, 10.2 mmole, 78%).

(*b*). *2-Butyne.* When a mixture of 2-butyne (0.82 g, 15.2 mmole) and hydridopentacarbonylmanganese (2.94 g, 15.0 mmole) were heated at 80° for 2 days in a tube sealed under vacuum, analysis of the reaction products by GLC after this period showed recovered 2-butyne (0.42 g, 7.78 mmole, 52%), *cis*-2-butene (0.35 g, 6.25 mmole, 43%), and *trans*-2-butene (0.04 g, 0.71 mmole, 5%); decacarbonyldimanganese (2.9 g, 7.40 mmole, 98%) was also obtained. When this reaction was carried out at room temperature no reaction occurred over 7 days.

(*c*). *3-Hexyne.* Hydridopentacarbonylmanganese (2.03 g, 10.4 mmole) and 3-hexyne (0.41 g, 5.0 mmole) heated in a tube *in vacuo* at 100° for 10 days gave

decacarbonyldimanganese (1.90 g, 4.85 mmole, 93%) and volatile products which were shown by GLC to consist of *cis*-3-hexene (0.31 g, 3.69 mmole, 75%), *cis*-2-hexene (0.05 g, 0.53 mmole, 11%), *trans*-3-hexene (0.04 g, 0.44 mmole, 9%) and *trans*-2-hexene (0.02 g, 0.25 mmole, 5%).

In a separate experiment it was shown that when hydridopentacarbonylmanganese (1.96 g, 10.0 mmole) and a mixture of *cis*- and *trans*-2-hexene [0.84 g, 10.0 mmole, containing *cis*-2-hexene (55%), *trans*-2-hexene (41%), n-hexane (2%) and *trans*-3-hexene (2%)] were heated under similar conditions to those described above, analysis of the product mixture showed recovered hydride (0.39 g, 2.0 mmole), decacarbonyldimanganese (1.50 g, 3.85 mmole, 77%), and a volatile fraction (0.75 g) which consisted of *trans*-2-hexene (0.35 g, 4.17 mmole, 42%), *cis*-2-hexene (0.25 g, 3.33 mmole, 33%), n-hexane (0.05 g, 0.61 mmole, 6%) and *trans*-3-hexene (0.10 g, 1.19 mmole, 12%).

(*d*). *Diphenylacetylene.* When hydridopentacarbonylmanganese (1.12 g, 5.17 mmole) and diphenylacetylene (0.93 g, 5.23 mmole) were mixed at room temperature *in vacuo* a rapid, exothermic reaction occurred over a period of ca. 10 min to give a red solid; no gas evolution took place during the reaction. Chromatographic separation (deactivated alumina) of the solid using light petroleum as the eluant gave decacarbonyldimanganese (1.0 g, 2.55 mmole, 89%), and a mixture shown by IR and ^{1}H NMR spectroscopy to contain diphenylacetylene (0.40 g, 2.25 mmole, 43%) and *trans*-stilbene (0.25 g, 1.39 mmole, 27%). Further elution with chloroform gave, after recrystallisation from carbon tetrachloride, white crystals of *trans*-2,3-diphenylacrolein (0.10 g, 0.48 mmole, 9%), m.p. 91–92° (reported[22] 94°). (Found: C, 86.4; H, 5.5. $C_{15}H_{12}O$ calcd.: C, 86.5; H, 5.8%.) Its ^{1}H NMR spectrum (in CCl_4; internal TMS) showed a singlet at τ 0.31 (–CHO) and a multiplet at τ 2.77 (aromatic protons + vinylic protons) in the intensity ratio of 1/11. The NMR and IR spectra were identical to those of an authentic sample prepared in 45% yield from benzaldehyde and phenylacetaldehyde[22].

Several attempts were made to repeat this reaction without success. When the reaction was carried out under more vigorous conditions the major reaction products were *trans*-stilbene and bibenzyl. The conditions used and the results of these experiments at room temperature and at 80° are given in the Table.

Reaction of hydridopentacarbonylmanganese and cis-stilbene

(*a*). *At room temperature.* A solution of hydridopentacarbonylmanganese (0.98 g, 5.0 mmole) and *cis*-stilbene (0.90 g, 5.0 mmole) in diethyl ether (15 ml) was kept at room temperature for 4 weeks in a tube sealed under vacuum. The volatile products were then transferred *in vacuo* to an external trap containing carbon tetrachloride (2 ml), and kept at room temperature for 15 min to give chloropentacarbonylmanganese (0.94 g, 4.08 mmole) corresponding to unreacted hydridopentacarbonylmanganese (0.8 g, 4.08 mmole, 82%). Chromatographic separation of the solid residue (1.0 g) in the tube on deactivated alumina using light petroleum as the eluant gave decacarbonyldimanganese (0.10 g, 0.26 mmole, 10%), and an oily liquid (0.8 g) shown by ^{1}H NMR spectroscopy to consist of unreacted *cis*-stilbene (0.55 g, 3.06 mmole, 61%), *trans*-stilbene (0.15 g, 0.83 mmole, 17%) and bibenzyl (0.05 g, 0.28 mmole, 6%).

(*b*). *At* 100°. When hydridopentacarbonylmanganese (0.47 g, 2.40 mmole) and

cis-stilbene (0.45 g, 2.50 mmole) were heated at 100° for 2 days, analysis of the reaction products by a similar procedure to that described above gave decacarbonyldimanganese (0.41 g, 1.15 mmole, 96%), *trans*-stilbene (0.18 g, 1.00 mmole, 40%) and bibenzyl (0.20 g, 1.10 mmole, 44%); no *cis*-stilbene could be detected among the reaction products. In a control experiment in which *cis*-stilbene was heated in the absence of hydride under similar conditions to those described above no isomerisation to *trans*-stilbene was observed.

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