Ruthenium(II)- and Rhenium(III)-catalysed Addition of Tetrahalogenomethanes to Alkenes and 1,ω-Dienes. Stereoselective Formation of *cis*-1,2-Disubstituted Cyclopentanes from 1,6-Dienes

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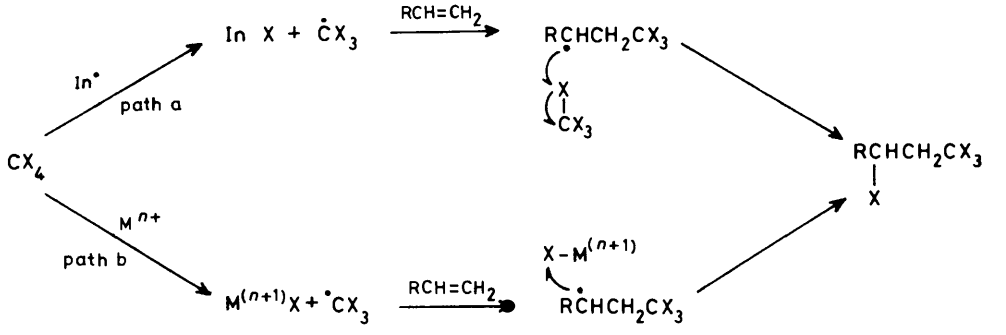
Acetonitrile(trichloro)bis(triphenylphosphine)rhenium(III) is found to act as an initiator for the addition of carbon tetrachloride and bromotrichloromethane to terminal alkenes and dienes. Moderate to good yields of mono- and bis-adducts are obtained. 1,6-Dienes undergo a stereoselective addition-cyclization process with both the Re^{III} catalyst and with dichlorotris(triphenylphosphine)ruthenium(II) to give mixtures of *cis*- and *trans*-3-halogenomethyl-4(2,2,2-trichloroethyl)cyclopentanes in which the *cis*-isomers predominate. The stereoselectivity is discussed and evidence presented for the Re^{III} complex acting as a simple initiator.

Free-radical initiators such as dibenzoyl peroxide or azo-isobutyronitrile (AIBN) effect the addition of tetrahalogenomethanes to alkenes to give 1,1,1,3-tetrahalogenoalkanes *via* a radical chain mechanism.[1] A range of transition metal (*e.g.* Cu, Fe, Co, Pd, Mo, Cr, and Ru) complexes and salts has also been found to act as catalysts for these addition reactions.[2–5]

Although the reactions catalysed by metal complexes and salts show evidence of proceeding *via* free radical intermediates, they frequently exhibit different features to the reactions initiated by AIBN or dibenzoyl peroxide. Thus AIBN or dibenzoyl peroxide initiate the addition of chloroform to terminal alkenes to give 1,1,1-trichloroalkanes whilst additions initiated by iron(II) salts give 1,1,3-trichloroalkanes.[6] Different products arise because the propagation steps in the two processes are different. In particular, when metal salts or complexes are used as initiators propagation may occur from a metal–halogen species (Scheme 1, path b) rather than from the polyhalogenomethane (Scheme 1, path a).

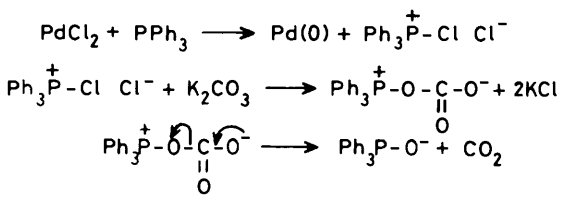


Scheme 1.

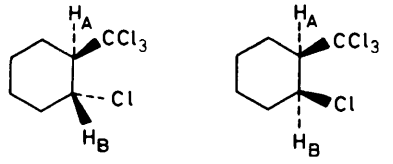
When metal complexes or salts are used as initiators their turnover capability is usually low but yields, calculated on the amount of alkene consumed, are often high. The most efficient metal complex initiator reported to date is Matsumoto's dichlorotris(triphenylphosphine)ruthenium(II).[4] Both yields and conversions, for the addition of carbon tetrachloride or chloroform to terminal alkenes are high with this catalyst whilst chlorotris(triphenylphosphine)rhodium(I), dichlorobis-(triphenylphosphine)palladium(II), and dichlorobis(triphenyl-phosphine)nickel(II) are less efficient initiators. Reactions initiated by the ruthenium(II) complex are inhibited by free radical scavengers such as galvinoxyl,[7] although radical scavengers do not always inhibit reactions initiated by metal species.[7,8] Tsuji has recently shown that a catalyst consisting of palladium acetate (1 mol%), triphenylphosphine (2 mol%), and potassium carbonate (200 mol%) effects the addition of tetrahalogenomethanes and methyl trichloroacetate to terminal alkenes in moderate to good yields.[9] A free radical mechanism with both carbon tetrachloride and palladium(I) chloride participating in the propagation of the chain reaction was suggested. The efficacy of potassium carbonate, compared with amines, as a 'base' in this reaction is probably due to its ability to function in an analogous manner to that suggested by us in the palladium acetate catalysed coupling of vinyl and aryl bromides,[10] *i.e.* to regenerate the catalytically active palladium(0) species from palladium(II) chloride according to Scheme 2.

The most striking differences reported for reactions involving activation by dichlorotris(triphenylphosphine)ruthenium(II) compared to activation by dibenzoyl peroxide concerns the addition of carbon tetrachloride to cyclohexene. The ruthenium(II) initiator is reported to be highly stereoselective and to give a 96:4 mixture of *trans*-(**1**) and *cis*-(**2**) adducts[11] whilst initiation with dibenzoyl peroxide gives a 53:47 mixture of (**1**) and (**2**).[12] Other differences include a marked variation in the ratio of 1,2- to 1,4-adducts arising from the addition of carbon tetrachloride to cyclo-octene depending on whether the process was initiated with the ruthenium(II) species or by conventional free radical initiators.[4] The contrasting results with the ruthenium(II) complex led Matsumoto *et al.* to suggest a chlororuthenium(III) species implicated in the propagation process (Scheme 1, path b). Recent kinetic studies[13] support this suggestion.

In contrast to other members of the third transition series



Scheme 2.



(1) (2)

examples of reactions catalysed by soluble rhenium complexes are comparatively rare. Rhenium pentachloride has been used as a metathesis catalyst [14] and the pentahydride has been used for the catalytic dehydrogenation of alkanes to alkenes.[15] We were attracted by a brief report that the rhenium(III) complex (3) reacts with carbon tetrachloride to give (4),[16] and have investigated the utility of (3) as an initiator for the free radical addition of tetrahalogenomethanes to alkenes and 1,ω-dienes.

$[ReCl_3(PPh_3)_2(MeCN)]$ (3) $[ReCl_4(Ph_3P)_2]$ (4)

(5) a R = n-C_4H_9; b R = n-C_5H_{11}; c R = $PhCH_2$

$RCH{=}CH_2$

$RCHCH_2CCl_3$ (6)
|
Cl

$(Ph_3P)_2ReCl_3$ (7)

$PhCH_2CHCH_2CCl_3$ (8)
|
Br

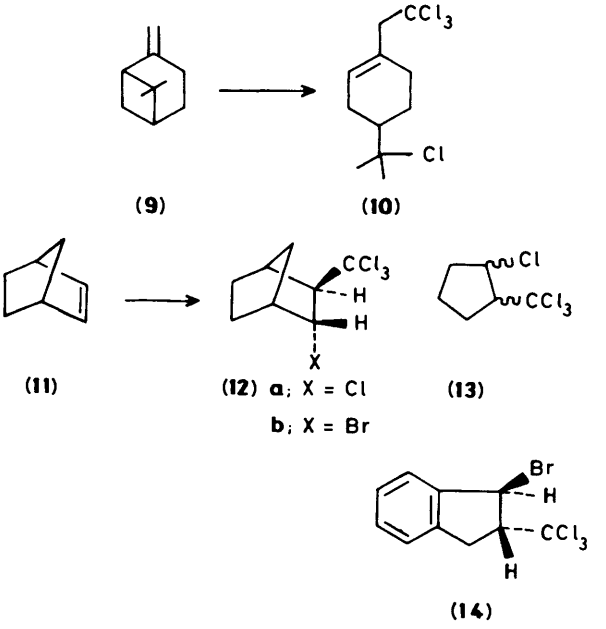
Boiling a dilute solution of (**5a**) in carbon tetrachloride containing 2 mol% of (**3**) resulted in a rapid initial reaction in which *ca.* 75% of the hex-1-ene was converted into (**6a**) in 15 min but only 80% conversion had occurred after 2 h. It seemed likely that the initiation step involved prior dissociation of acetonitrile from (**3**) to give the five co-ordinate complex (**7**) which upon abstraction of chlorine atom from carbon tetrachloride gave (**4**). Thus addition of an excess of acetonitrile should control the rate of production of trichloromethyl radicals by depressing the dissociation of acetonitrile from (**3**). It was found that addition of a 12.5 mol excess of acetonitrile with respect to catalyst resulted in complete consumption of alkene within 2 h in most instances. Under these conditions terminal alkenes (**5a**—**c**) treated with carbon tetrachloride or bromotrichloromethane gave the 1:1 adducts (**6a**,**b**) and (**8**) in good yield (Table 1). The strained alkenes (**9**) and (**11**) give moderate yields of 1:1 adducts (**10**) and (**12a**,**b**) respectively (Table 1). Much better yields of (**10**)[17] and (**12a**,**b**)[18] are obtained using conventional free-radical initiators. The adducts (**12a**,**b**) are assigned *trans*-stereochemistry based on comparisons of their n.m.r. spectra with literature data.[18]

The rhenium catalyst is ineffective for the addition of carbon tetrachloride to internal alkenes. Using conditions analogous to those of Table 1 but with cyclohexene as the substrate, the reaction only went to 20% completion and gave a 5% yield of 55:45 mixture of (**1**) and (**2**). Product stereochemistry in this case was assigned on the basis of the magnitude of the ^1H n.m.r. coupling constants $J_{H_AH_B}$ [(**1**), 5 Hz; (**2**), 2.5 Hz]. Although the yield in the case of cyclohexene is very low, the *trans*:*cis* product ratio is identical, within experimental error, to that

Table 1. Addition of tetrahalogenomethanes to alkenes catalysed by 2 mol% of (3)[a]

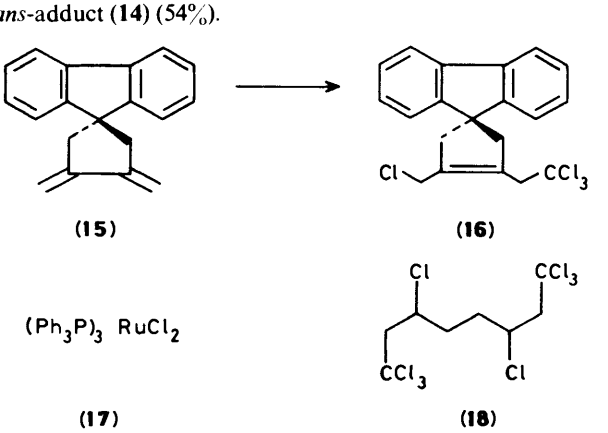
Substrate	Product	Yield (%)[b]
(**5a**)	(**6a**)	76
(**5b**)	(**6b**)	76
(**5c**)	(**8**)	77
(**9**)	(**10**)	46
(**11**)	(**12a**)	39
(**11**)	(**12b**)	44

[a] All reactions were carried out for 2 h in an excess of boiling carbon tetrachloride or bromotrichloromethane containing 25 mol% acetonitrile. [b] Isolated yields.



(9) (10) (11) (12) a; X = Cl b; X = Br (13) (14)

obtained from a dibenzoyl peroxide initiated reaction but differs markedly from that (96:4) obtained by Matsumoto *et al.* from the ruthenium(II) initiated reaction.* Thus although we have not carried out a detailed mechanistic study we believe the rhenium complex (**3**) functions as a simple radical chain initiator with the excess of acetonitrile controlling the initiation process by influencing the equilibrium (**3**) $\rightleftharpoons$ (**7**). Cyclopentene reacted similarly to cyclohexene to give a low yield of (**13**) (21%) and indene and bromotrichloromethane gave the *trans*-adduct (**14**) (54%).



(15) (16) $(Ph_3P)_3RuCl_2$ (17) (18)

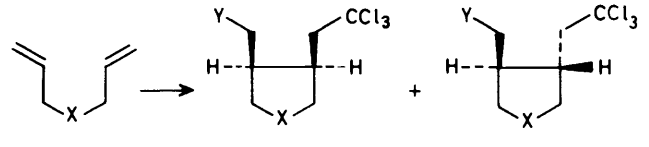
* In our hands Matsumoto's reaction gave an 84:16 *trans*:*cis* adduct ratio.

Table 2. Addition of carbon tetrachloride and bromotrichloromethane to 1,6-dienes catalysed by metal complexes (**3**) and (**17**)[a]

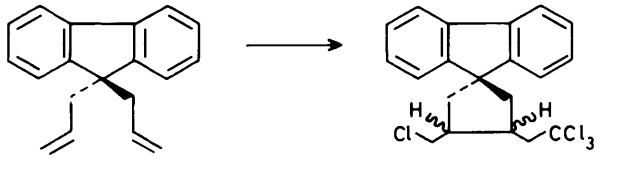
Substrate	Catalyst	Reaction time (h)	Product(s)	Y	Product *cis*:*trans* ratio	Yield (%)[b]
(**19a**)	(**3**)	2	(**20**),(**21**)	Cl	5:1	74
(**19a**)	(**3**)	2	(**20**),(**21**)	Br	5.2:1	82
(**19b**)	(**3**)	2	(**20**),(**21**)	Cl	4.2:1	73
(**19b**)	(**3**)	2	(**20**),(**21**)	Br	2.8:1	61
(**19d**)	(**3**)	2	(**20**),(**21**)	Cl	4.3:1	87
(**19e**)	(**3**)	2	(**20**),(**21**)	Cl	6:1	64
(**22**)	(**3**)	10	(**23**)	Cl	4.2:1	79
(**19a**)	(**17**)	16	(**20**),(**21**)	Cl	*c*	86,5
(**19b**)	(**17**)	30	(**20**),(**21**)	Cl	3.2:1	84
(**19b**)	(**17**)	2	(**20**),(**21**)	Br	2.6:1	73
(**19c**)	(**17**)	14	(**20**),(**21**)	Cl	*c*	65
(**19e**)	(**17**)	8	(**20**),(**21**)	Cl	6:1	77
(**24**)	(**17**)	30	(**25**)	Cl	*c*	48

[a] Reactions carried out in boiling carbon tetrachloride using 2 mol% of (**3**) or 5 mol% of (**17**). [b] Isolated yields. [c] Isomer ratio not determined.

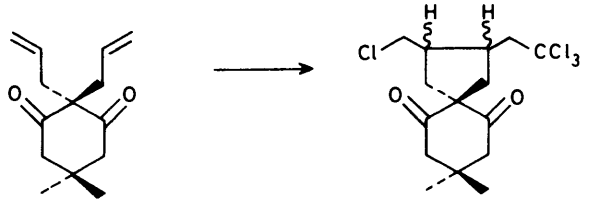
The ruthenium(II)- and rhenium(III)-catalysed addition of carbon tetrachloride to a range of 1,ω-dienes has also been studied. The rhenium complex (**3**) is an efficient catalyst for the 1,4-addition of carbon tetrachloride to the 1,3-diene (**15**) to give (**16**) (67%). Hexa-1,5-diene reacted slowly and incompletely over 27 h in the presence of the ruthenium(II) catalyst (**17**) to give the 2:1 adduct (**18**) (35%).



(**19**) **a** X = $C(CO_2Et)_2$ (**20**) (**21**)
b X = $C(COPh)_2$
c X = $C(COMe)_2$
d X = O
e X = NCOMe



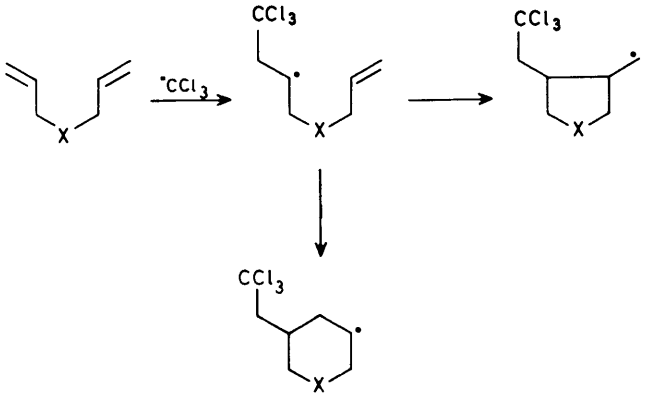
(**22**) (**23**)



(**24**) (**25**)

We have previously reported the palladium(II)- and Rh(I)-catalysed cyclisations of hepta-1,6-dienes to cyclopentenes and methylene cyclopentanes respectively[19] and it was therefore of interest to look at the metal ion-induced radical cyclisations of these substrates. Treatment of the 1,6-dienes (**19a**,**b**, and **d**), (**22**), and (**24**) with the rhenium(III) catalyst (**3**) (2 mol%) under the usual conditions (boiling carbon tetrachloride, 25 mol% acetonitrile) gave mixtures of the isomeric cyclopentanes (**20**) and (**21**), and (**23**) and (**25**) respectively in high yield (Table 2). The ruthenium catalyst (**17**) also effected analogous cyclisations (Table 2).

The cyclisation of unstabilised hex-5-enyl radicals to cyclopentylmethyl radicals (5-*exo*-*trig* cyclisation) rather than cyclohexyl radicals (6-*endo*-*trig* cyclisation) (Scheme 3) is well



Scheme 3.

known[20] and various explanations for the observed regiospecificity have been advanced including entropic,[21] steric,[22] and stereoelectronic factors.[23]

The most satisfying explanation of the regiospecific cyclisation of hex-5-enyl radicals to cyclopentylmethyl radicals (5-*exo*-*trig* cyclisation) and of hex-5-enyl carbonium ions to cyclohexyl carbonium ions (6-*endo*-*trig* cyclisation) is provided by consideration of stereoelectronic factors. The radical cyclisation involves attack of the singly occupied molecular orbital (SOMO) of the radical on the olefin LUMO (π*). Repulsion between the SOMO and part of the LUMO [Figure 1(a)] results in an inclined angle of approach (θ ≃ 105°) that geometrically favours a five-membered transition state. In contrast the corresponding cationic cyclisation involves interaction of the carbonium ion LUMO (vacant p orbital) with the alkene HOMO (π). Attraction between the p orbital and the HOMO [Figure 1(b)] results in an attack angle θ of *ca.* 70° leading to a six-membered product.

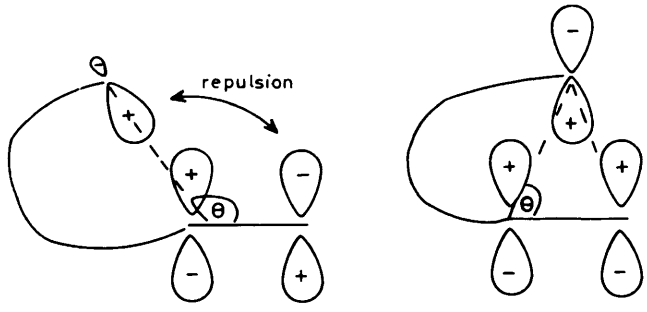
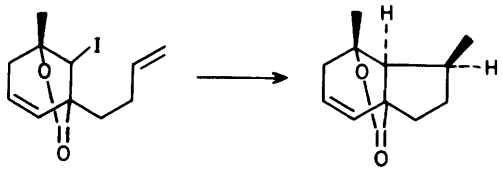


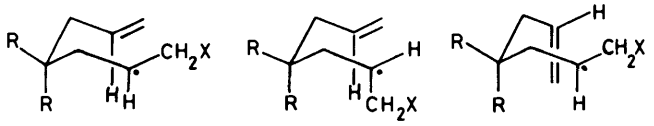
Figure 1: (a) Intramolecular cyclisation of a hex-5-enyl radical. (b) Intramolecular cyclisation of a hex-5-enyl carbonium ion

The regiospecific radical cyclisation of (**19a**—**e**) is also strongly stereoselective for the *cis*-isomers (**20**). In contrast, the dibenzoyl peroxide initiated addition of carbon tetrachloride to (**19a**) has been reported to give the *trans* isomer (**21a**) as the major product[24] and other analogous reactions with *cis*:*trans* ratios of *ca.* 1:5 have been reported.[25] However, these assignments are questionable, and recent work confirms a strong

preference for the *cis*-isomer. Thus the cyclisation of (**19d**) using perfluoroalkyl iodides as the addenda[26] occur with mainly *cis*-stereoselectivity and similar stereoselectivity is observed in the cyclisation of thiols[27] and in the radical cyclisation of (**26**) to (**27**).[28] In general, 1-substituted hex-5-enyl radicals give predominantly *cis*-1,2-disubstituted cyclopentenes on cyclisation.[29]



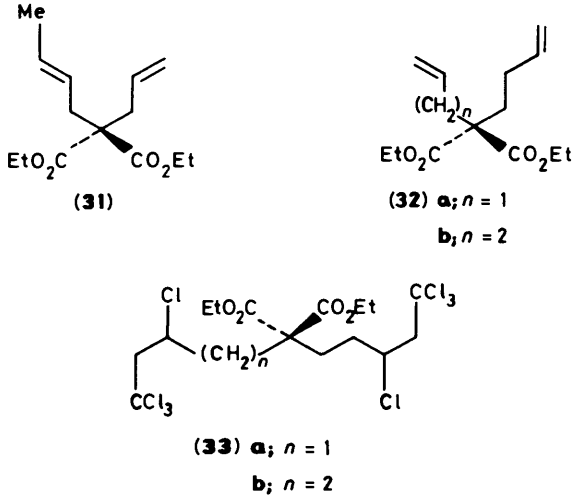
(**26**) (**27**)



(**28**) (**29**) (**30**)

It seems probable that the *cis*-stereoselectivity observed in our cyclisations (Table 2) reflects steric effects in the transition state. Thus (**28**) has two 1,3-pseudo diaxial interactions between R and H whilst (**29**) and (**30**) have one R/H interaction and one more severe interaction involving R/CH_2X or R/C=CH_2 respectively. This argument, based on conformational preferences, also rationalises the cyclisation of 2-substituted hex-5-enyl radicals to *cis*-1,3-disubstituted cyclopentanes and of 4-substituted 5-hexen-1-yl radicals to *trans*-1,2-disubstituted cyclopentanes.[30]

The assignment of *cis*-stereochemistry (**20**) to the major isomers from our radical addition-cyclisation reactions was made on the basis of n.m.r. data. Thus the ^{13}C DEPT n.m.r. spectrum of the mixture of isomers (**20a**; Y = Cl) and (**21a**; Y = Cl) from (**19a**) gave the multiplicity of the various ^{13}C signals and allowed identification of the CH_2Cl and CH_2CCl_3 carbon atoms. A ^{13}C–^1H shift correlated 2D n.m.r. spectrum then allowed assignment of ^{13}C signals to the major and minor isomer. Finally, the stereochemistry was assigned on the basis of the γ-effect[31] whereby a carbon *cis* to another carbon at the γ-position suffers extra shielding in the ^{13}C n.m.r. spectrum as compared with a *trans* carbon. Thus the chemical shifts for CH_2Cl in (**20a**; Y = Cl) and (**21a**; Y = Cl) are 44.8 and 46.1 p.p.m. respectively and 54.34 and 59.4 p.p.m. for CH_2CCl_3.



(**31**) (**32**) **a**; *n* = 1 **b**; *n* = 2

(**33**) **a**; *n* = 1 **b**; *n* = 2

The terminally substituted 1,6-diene (**31**) reacted with carbon tetrachloride in the presence of the ruthenium catalyst (**17**) to give a mixture (63%) of cyclic 1:1 adducts. The 1,7-diene (**32a**) and the 1,8-diene (**32b**) reacted with carbon tetrachloride in the presence of a catalytic amount of (**17**) to give the acyclic 2:1 adducts (**33a**) (29%) and (**33b**) (98%) respectively.

Under similar conditions to those discussed above, the rhenium(III) catalyst (**3**) did not effect the addition of chloroform, bromoform, phenacyl chloride, or diethyl trichloromethane phosphonate to terminal alkenes.

Experimental

N.m.r. spectra were recorded on JEOL PMX60, Bruker WH90, or Bruker WP250 instruments and refer to deuteriochloroform solutions, with tetramethylsilane as internal standard, unless otherwise stated. I.r. spectra were measured for KBr discs on a Perkin-Elmer 457 instrument. Mass spectra were determined on an MS902 operating at 70 eV. M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer PE240 automatic analyser. Sodium perrhenate was supplied by Thiokol, Ventron Division and was converted to acetonitrilebis(triphenylphosphine)-rhenium(III) trichloride (**3**) by the literature procedure.[16] Light petroleum refers to the fraction b.p. 40—60 °C and silica refers to silica gel G (Merck).

Addition of Tetrahalogenomethanes to Alkenes.—General Procedure. Acetonitrile(trichloro)bis(triphenylphosphine)-rhenium(III) (2 mol%) was added to a degassed solution of the alkene (1 g) in carbon tetrachloride or bromotrichloromethane (25 ml) containing acetonitrile (25 mol%) and the solution was then boiled under reflux for 2 h. The insoluble red material [$(Ph_3P)_2ReCl_4$] was filtered off and the filtrate evaporated to dryness. The residue was triturated with ether–light petroleum to precipitate any remaining catalyst and then passed through a short column of silica.

1,1,1,3-*Tetrachloroheptane* (**6a**). Distillation of the crude oil gave the product (2.18 g, 76%) as a colourless oil, b.p. 37—39 °C/0.5 mmHg (lit.,[32] b.p. 108 °C/10 mmHg); δ 4.24 (m, 1 H, CHCl), 3.27 and 3.13 (2 × q, 2 × 1 H, CH_2CCl_3), 1.89 (m, 2 H, CH_2CHCl), 1.48 (m, 4 H, 2 × CH_2), and 0.94 (t, 3 H, Me).

1,1,1,3-*Tetrachloro-octane* (**6b**). The product (1.87 g, 73%) distilled as a colourless oil, b.p. 88—90 °C/2.5 mmHg (lit.,[33] 112—114 °C/10 mmHg); δ 4.24 (m, 1 H, CHCl), 3.27 and 3.11 (2 × m, 2 × 1 H, CH_2CCl_3), 1.89 (m, 2 H, CH_2CHCl), 1.56 (m, 2 H), 1.48 (m, 4 H, 2 × CH_2), and 0.94 (t, 3 H, Me).

3-*Bromo*-1,1,1-*trichloro*-4-*phenylbutane* (**8**). The product (2.05 g, 77%) distilled as a colourless oil, b.p. 120—124 °C/1.5 mmHg (Found: C, 38.35; H, 3.30. $C_{10}H_{10}BrCl_3$ requires C, 37.95; H, 3.20%); δ 7.4 (m, 5 H, ArH), 4.5 (m, 1 H, CHBr), 3.45 (dd, 2 H, CH_2CCl_3), and 3.25 (dd, 2 H, $ArCH_2$); $\nu_{max.}$(film) 3 040, 3 020, 2 920, 1 495, 1 455, 1 155, 1 080, 950, 790, and 750 cm^{-1}.

1-(2,2,2-*Trichloroethyl*)-4-(2-*chloroisopropyl*)*cyclohex*-1-*ene* (**10**). Prepared from β-pinene as a colourless oil (0.95 g, 45%), b.p. 88—92 °C/0.04 mmHg (lit.,[17] m.p. 46—46.5 °C); δ 5.81 (t, 1 H, C=CH), 3.35 (s, 2 H, CH_2CCl_3), 2.40 (m, 2 H), 2.0 (m, 4 H, 2 × CH_2), 1.88 (m, 1 H), and 1.60 and 1.56 (2 × s, 2 × Me).

endo-3-*Chloro*-exo-2-*trichloromethylbicyclo*[2.2.1]*heptane* (**12a**). The product (1.61 g, 59%) was obtained as a colourless oil, b.p. 92—96 °C/1.8 mmHg (lit.,[18,34] 75—76 °C/0.4 mmHg); δ 4.24 (m, 1 H, CHCl), 2.65 (m, 2 H, $CHCCl_3$ and bridgehead H), 2.53 (s, 1 H, bridgehead H), 2.08 (m, 2 H, bridge CH_2), and 1.74—1.34 (m, 4 H, 2 × CH_2). G.l.c. of the product (150 °C, 2 m 2.5% SGR) showed the presence of 5% of an isomeric adduct.

endo-3-*Bromo*-exo-2-*trichloromethylbicyclo*[2.2.1]*heptane* (**12b**). Distillation afforded the product (1.35 g, 44%) as a colourless oil, b.p. 118—122 °C/1.0 mmHg (lit.,[18,34] 88—

89 °C/0.3 mmHg); δ 4.29 (m, 1 H, CHBr), 2.74 (m, 1 H, $CHCCl_3$), 2.62 and 2.55 (2 × br s, 2 × 1 H, bridgehead H), 2.15 (m, 2 H, CH_2 bridge), and 1.64 and 1.39 (2 × m, 2 × 2 H, 2 × CH_2). G.l.c. analysis of the product (150 °C, 2 m, 2.5% SGR) showed the presence of 4% of an isomeric adduct.

1-*Chloro*-2-*trichloromethylcyclopentane* (**13**).[35] The product (0.61 g. 21%) distilled as a colourless oil, b.p. 60—63 °C/2.5 mmHg; δ 1.39—2.36 (m, 6 H, ring CH_2), 3.49 (m, 1 H, $CHCCl_3$), and 4.46 (m, 1 H, CHCl).

trans-1-*Bromo*-2-*trichloromethylindan* (**14**). Obtained as a colourless oil (1.50 g, 54%), b.p. 105—109 °C/0.5 mmHg (lit.,[18] 125—129 °C/0.1 mmHg); δ 3.37 (m, 2 H, CH_2), 3.95 (m, 1 H, $CHCCl_3$), 5.55 (m, 1 H, CHBr), and 7.25 (m, 4 H, ArH).

Addition of Tetrahalogenomethanes to 1,ω-*Dienes.—General Procedure*. (A) Rhenium(III) initiated reactions were performed as described above for alkenes. (B) Ruthenium(II). A solution (6—20%, w/w) of the 1,ω-diene in carbon tetrachloride or bromotrichloromethane containing dichlorotris(triphenylphosphine)ruthenium(II) (5 mol% based on diene) was boiled under reflux. The reaction was monitored by g.l.c. (5% SGR 2 m, or 2.5% CEMS 4 m). At the end of the reaction the solvent was removed under reduced pressure, and residue triturated with light petroleum to precipitate ruthenium salts and filtered through a short silica column. The filtrate was evaporated and the residue distilled or crystallised as appropriate.

3-*Chloromethyl*-4-(2,2,2-*trichloroethyl*)*spiro*[*cyclopent*-3-*ene*-1,9′-(9H)*fluorene*] (**16**). The product (67%), prepared by method (A), crystallised from light petroleum as colourless prisms, m.p. 125—127 °C (Found: C, 60.05; H, 4.30; Cl, 35.65. $C_{20}H_{16}Cl_4$ requires C, 60.35; H, 4.05; Cl, 35.60%); *m/z* (%) 402 (13), 400 (49), 398 (100), and 396 (73) (M^+, Cl isotopes); δ 7.68 and 7.52 (2 × d, 2 × 2 H, Ar H), 7.30 (m, 4 H, ArH), 4.36 (s, 2 H, CH_2Cl), 3.71 (s, 2 H, CH_2CCl_3), and 3.24 and 3.10 (2 × s, 2 × 2 H, 2 × CH_2).

2,5-*Dichloro*-1,6-*bis*(*trichloromethyl*)*hexane* (**18**). The reaction was complete after 27 h using method (B). The product (35%) crystallised from light petroleum as colourless needles, m.p. 74—75 °C (lit.,[36] 72—74 °C); δ 1.98 (m, 2 H), 2.35 (m, 2 H), 3.15 and 3.33 (2 × m, 2 × 2 H, 2 × CH_2CCl_3), and 4.30 (m, 2 H, 2 × CHCl).

cis- *and* trans-*Diethyl* 3-*chloromethyl*-4-(2,2,2-*trichloroethyl*)-*cyclopentane*-1,1-*dicarboxylate* (**20a**; Y = Cl) *and* (**21a**; Y = Cl). Prepared (74%) by method (A) as a golden viscous oil, b.p. 135—140 °C/0.05 mmHg and by method B (86.5%) as a colourless viscous oil, b.p. 150—152 °C/0.1 mmHg (lit.,[24] b.p. 149—155 °C/0.15 mmHg) (Found: C, 42.35; H, 5.10. Calc. for $C_{14}H_{20}Cl_4O_4$: C, 42.65; H, 5.05%); δ 1.26 (2 × t, 2 × 3 H, CH_2Me), 2.26—2.64 (4 × q, 4 H, ring CH_2), 2.76, 2.98 (2 × m, *AB*X multiplet, 2 H, CH_2CCl_3), 3.48, 3.64 (2 × m, *AB*X multiplet, 2 H, CH_2Cl), and 4.23 (2 × q, 2 × 2 H, CH_2Me).

cis- *and* trans-*Diethyl* 3-*bromomethyl*-4-(2,2,2-*trichloroethyl*)-*cyclopentane*-1,1-*dicarboxylate* (**20a**; Y = Br) *and* (**21a**; Y = Br). Prepared (82%) by method A as a colourless oil, b.p. 176—182 °C/0.4 mmHg (Found: C, 38.55; H, 4.40. $C_{14}H_{20}BrCl_3O_4$ requires C, 38.35; H, 4.6%); δ 1.26 (t, 6 H, 2 × CH_2Me), 2.50 (m, 6 H, ring CH and CH_2), 2.98 (m, 2 H, CH_2CCl_3), 3.50 (q, 2 H, CH_2Br) (major isomer), 3.60 (q, 2 H, CH_2Br) (minor isomer), and 4.20 (q, 4 H, CH_2Me). The *cis*:*trans* isomer ratio was calculated as 84:16 by integration of the n.m.r. spectrum.

Using method (B) the yield was 71% of an 82:18 *cis* and *trans* mixture.

cis- *and* trans-1,1-*Dibenzoyl*-3-*chloromethyl*-4-(2,2,2-*trichloroethyl*)*cyclopentane* (**20b**; Y = Cl) *and* (**21b**; Y = Cl). Prepared (73%) as a 4.2:1 mixture (n.m.r.) of *cis* and *trans* isomers using method (A). The gummy white solid crystallised from acetonitrile to give the pure *cis*-isomer (**20b**) (0.51 g, 32%) as colourless needles, m.p. 97 °C (Found: C, 57.75; H, 4.50. $C_{22}H_{20}Cl_4O_2$ requires C, 57.65; H, 4.35%); δ 2.72 (m, 6 H, ring CH and CH_2), 2.96 (2 × q, 2 H, CH_2CCl_3), 3.45 and 3.65 (2 × q, 2 H, CH_2Cl), 7.30 (m, 6 H, ArH), and 7.78 (d, 4 H, ArH); $\nu_{max.}$ 3 040, 2 900, 1 650, 1 590, 1 060, 925, and 690 cm^{-1}.

The mother liquor from the crystallisation was evaporated to give a froth and separated by preparative h.p.l.c. (7 μm Lichrosorb Si60, 16 mm × 25 cm column, flow rate 15 ml/min) eluting with 20:1 hexane–ether. The *trans*-isomer (**21b**) was obtained as an oil which failed to crystallise; δ 2.57 (m, 6 H, ring CH and CH_2), 3.03 and 3.28 (2 × q, 2 H, CH_2CCl_3), 3.58 and 3.76 (2 × q, 2 H, CH_2Cl), 7.39 (m, 6 H, ArH), and 7.78 (m, 4 H, ArH); $\nu_{max.}$ 2 900, 1 660, 1 590, 1 050, and 800 cm^{-1}.

Using method (B) the reaction took 30 h and afforded a 3.2:1 mixture of *cis*- and *trans*-isomers (1.34 g, 84%).

cis- *and* trans-1,1-*Dibenzoyl*-3-*bromomethyl*-4-(2,2,2-*trichloroethyl*)*cyclopentane* (**20b**; Y = Br) *and* (**21b**; Y = Br). Prepared (61%) by method (A) as a 2.8:1 mixture of *cis*- and *trans*-isomers (n.m.r.). The crude product was a brown solid, m.p. 66—72 °C, and was purified by precipitation as an amorphous colourless solid from methylene dichloride by ether–pentane (Found: C, 51.95; H, 4.0. $C_{22}H_{20}BrCl_3O_2$ requires C, 52.5; H, 4.00%); δ 2.65 (m, 6 H, ring CH and CH_2), 3.03 (m, 2 H, CH_2CCl_3), 3.51 (2 × q, 1 H, CH_2Br) (major and minor isomer), 3.67 (q, 1 H, CH_2Br) (major isomer), 3.74 (q, 1 H, CH_2Br) (minor isomer), and 7.43 and 7.75 (2 × m, 10 H, ArH); $\nu_{max.}$ 3 040, 2 900, 1 640, 1 620, 1 580, 1 060, and 930 cm^{-1}.

Method (B), using 5 mol% catalyst, and a 2 h reaction time, gave the product (73%) as a brown solid, m.p. 58—64 °C, which comprised a 2.6:1 mixture of *cis*- and *trans*-isomers.

cis- *and* trans-1,1-*Diacetyl*-3-*chloromethyl*-4-(2,2,2-*trichloroethyl*)*cyclopentane* (**20c**; Y = Cl) *and* (**21c**; Y = Cl). Prepared (65%) by method (B) and obtained as a colourless oil, b.p. 140—144 °C/0.1 mmHg (Found: C, 43.5; H, 5.15. $C_{12}H_{16}Cl_4O_2$ requires C, 43.15; H, 4.85%); δ 2.14 (s, 6 H, 2 × Me), 2.49 (m, 6 H, ring CH and CH_2), 2.90 (m, 2 H, CH_2CCl_3), and 3.32 and 3.63 (2 × q, 2 H, AB portion of ABX system, CH_2Cl); $\nu_{max.}$(film) 2 960, 1 690, 1 420, 1 350, 1 200, 1 150, 950, 740, and 690 cm^{-1}.

cis- *and* trans-3-*Chloromethyl*-4-(2,2,2-*trichloroethyl*)*tetrahydrofuran* (**20d**; Y = Cl) *and* (**21d**; Y = Cl). Using method (A) the product (87%) was obtained as a colourless oil, b.p. 80—84 °C/0.01 mmHg (lit.,[37] b.p. 70—72 °C/0.1 mmHg) which comprised a 4.2:1 mixture of *cis*- and *trans*-isomers; δ 2.70 (m, 2 H, 2 × CH), 3.60 (m, 4 H, 2 × CH_2O), 3.90 (m, 2 H, CH_2CCl_3), and 4.19 and 3.93 (2 × q, 2 H, CH_2Cl); $\nu_{max.}$(film) 2 970, 2 860, 1 064, and 929 cm^{-1}.

cis- *and* trans-N-*Acetyl*-3-*chloromethyl*-4-(2,2,2-*trichloroethyl*)*pyrrolidine* (**20e**; Y = Cl) *and* (21e; Y = Cl). Prepared by methods (A) (64%) and (B) (77%) as a brown solid, m.p. 62—68 °C, which comprised a 6:1 mixture of *cis*- and *trans*-isomers (integration of COMe signal in n.m.r. spectrum). Crystallisation from ether gave the pure *cis*-isomer (**20e**; Y = Cl) as colourless rods, m.p. 81—83 °C (Found: C, 37.0; H, 4.4; N, 4.7. $C_9H_{13}Cl_4NO$ requires C, 36.90; H, 4.45; N, 4.80%); δ 2.08 (s, 3 H, COMe), 2.81 and 2.95 (2 × m, 2 × 2 H, CH_2N), 3.46 (m, 2 H, CH_2CCl_3), 3.67 (m, 3 H, 2 × CH and CHCl), and 3.91 (m, 1 H, CHCl); $\nu_{max.}$ 2 950, 2 920, 2 860, 1 615, 1 440, 895, 842, 800, and 780 cm^{-1}.

cis- *and* trans-3-*Chloromethyl*-4-(2,2,2-*trichloroethyl*)*spiro*-[*cyclopentane*-1,9′-(9H)*fluorene*] (**23**). Method (A) afforded the product (79%) as a brown solid, m.p. 114—118 °C which comprised a 4.2:1 mixture of *cis*- and *trans*-isomers of (**23**) (estimated by h.p.l.c., below). Crystallisation from acetone gave the pure cis-isomer as colourless prisms, m.p. 123—124 °C (Found: C, 59.9; H, 4.5; Cl, 35.6. $C_{20}H_{18}Cl_4$ requires C, 60.05; H, 4.55; Cl, 35.45%); δ 2.75 (m, 6 H, 2 × CH and 2 × CH_2), 3.27 (2 × q, 2 H, CH_2CCl_3), 3.88 (2 × q, 2 H, CH_2Cl), 7.31 (m, 4 H, ArH), and 7.49 and 7.71 (2 × m, 2 × 2 H, ArH).

H.p.l.c. analysis (partisil, hexane, 1 ml/min) of the crude pro-

duct (above) showed it to consist of a 4.2:1 mixture of *cis*- and *trans*-(**23**). Preparative h.p.l.c. afforded the minor isomer as colourless solid m.p. 116—118 °C; δ 2.29 (m, 6 H, ring CH and CH_2), 2.81 and 3.16 (2 × q, 2 H, CH_2CCl_3), 3.60 and 3.74 (2 × q, 2 H, CH_2Cl), and 7.21—7.66 (m, 8 H, ArH).

3-(2,2,2-*Trichloroethyl*)-2-*chloromethylspiro*[4.5]*decane*-6,10-*dione* (**25**). Prepared by method (B). Crystallisation of the crude reaction product from light petroleum (b.p. 40—60 °C) afforded (**25**) (48%) as colourless prisms, m.p. 82—85 °C (Found: C, 47.9; H, 5.6. $C_{15}H_{20}Cl_4O_2$ requires C, 48.10; H, 5.30%); δ 0.98 and 1.04 (2 × s, 6 H, Me), 2.20—2.50 (4 × q, overlapping, 4 H, cyclopentane ring CH_2), 2.58—2.70 (m, 4 H, CH_2CO), 2.76 and 2.94 (2 × q, 2 H, AB portion of ABX system, CH_2CCl_3), and 3.43 and 3.65 (2 × q, 2 H, CH_2Cl); $\nu_{max.}$ 2 940, 1 715, 1 685, 1 450, 1 320, 1 300, 1 245, 1 070, 950, 810, and 770 cm^{-1}.

Diethyl 2,7-*dichloro*-1,8-*bis*(*trichloromethyl*)*octane*-4,4-*dicarboxylate* (**33a**). Prepared by method (B) as a colourless semisolid material, b.p. 200—210 °C/0.05 mmHg, which on crystallisation from hexane afforded (**33a**) (29%) as colourless needles, m.p. 69—71 °C (Found: C, 34.4; H, 4.05; Cl, 50.35. $C_{16}H_{22}Cl_8O_4$ requires C, 34.20; H, 3.95; Cl, 50.45%); δ 1.27 (overlapping t, 6 H, 2 × CH_2Me), 1.88 (m, 2 H, CH_2), 2.19, 2.35, 2.62, and 2.72 (4 × m, 4 H, 2 × CH_2CHCl), 3.26 (4 × m, 4 H, 2 × CH_2CCl_3), 4.21 (overlapping q, 4 H, 2 × CH_2Me), and 4.33 (m, 2 H, 2 × CHCl); $\nu_{max.}$ 2 980, 2 925, 2 900, 1 715, 1 210, 1 185, 960, and 925 cm^{-1}.

Diethyl 2,8-*dichloro*-1,9-*bis*(*trichloromethyl*)*nonane*-5,5-*dicarboxylate* (**33b**). Using method (B) the product (98%) was obtained as colourless rods, m.p. 84—85 °C, from hexane (Found: C, 35.6; H, 4.3. $C_{17}H_{24}Cl_8O_4$ requires C, 35.45; H, 4.20); δ 1.27 (t, 6 H, 2 × CH_2Me), 1.81 and 2.21 (2 × m, 4 H, 2 × CH_2CHCl), 2.03 (m, 4 H, 2 × CH_2), 3.13 and 3.30 (2 × m, 4 H, 2 × CH_2CCl_3), and 4.23 (m, 6 H, 2 × CH_2Me and 2 × CHCl); $\nu_{max.}$ 2 910, 1 712, 1 258, 1 180, 1 090, 1 020, and 775 cm^{-1}.

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