Lewis Acid Catalysis of the Ene Addition of Chloral and Bromal to Olefins; Product Studies

Jill P. Benner, G. Bryon Gill,* Stephen J. Parrott, and Brian Wallace
Department of Chemistry, The University, Nottingham NG7 2RD

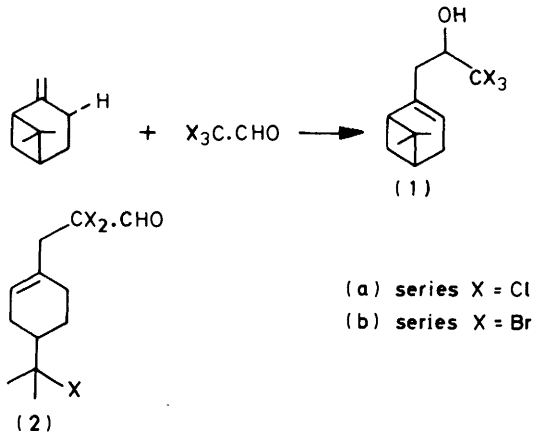
The addition of chloral and bromal to a variety of alkyl-substituted alkenes has been investigated. The effect on the reaction of varying the Lewis acid catalyst and the structure of the substrate have been studied. Anhydrous $AlCl_3$ was found to be the most effective catalyst, and ene-type adducts were the major products in most cases. Side reactions were observed with the less reactive systems leading, variously, to the formation of trihalogenoketones, hydrohalogenated ene adducts, and cyclic ethers. Conditions for optimising the yield of ene adducts were established in some cases. The trihalogenoketone by-products can be conveniently removed by a Grignard-type reaction.

Since ene reactions [1] involve σ as well as π-bond cleavage, activation energies are higher than those for related Diels–Alder reactions, and forcing conditions (*e.g.* $T > 250$ °C) are generally necessary except when the enophile is particularly reactive. Accordingly, there has been much interest in the catalysis of ene reactions by Lewis acids.[2,3] These developments have largely followed upon earlier observations that Lewis acids could, in suitable circumstances, greatly (*ca.* 10^6) enhance the rates of Diels–Alder reactions with marked improvement in the regio- and stereo-selectivity of the processes.[4] The function of the Lewis acid appears to be to co-ordinate a Lewis base site (usually an O atom) close to the reactive unsaturated centre of the (di)enophile, thereby making it more electrophilic.

We have undertaken a basic systematic study of the catalysis of ene reactions. In order to help define the horizons in this area as economically as possible our initial investigations were limited to the enophile chloral, and the effect on the reaction of variations in the other main parameters (the olefin substrate, Lewis acid, and reaction conditions) have been studied in some detail. In appropriate cases comparisons have been made with the corresponding reactions of bromal. The stereochemical and mechanistic aspects of this investigation are reported in the following paper [5a] which itself precedes the results of our studies into the chemistry of the ene adducts.[5b]

Colonge and Perrot [6a] studied the $AlCl_3$-catalysed addition of chloral to various olefins. On the basis of i.r. spectra and degradative studies the products were identified as arising from Friedel-Crafts substitution. However, Normant and Ficini [7a] prepared [$Me_2C{=}CHCH(OH)CCl_3$] by an independent route and showed, by physical comparisons, it to be not identical with the product reported for the 2-methylpropene–chloral reaction under $AlCl_3$ catalysis. Colonge and Perrot [6b] then amended their formulation to a 70 : 30 mixture of the above and the ene type adduct [$H_2C{=}C(Me)CH_2CH(OH)CCl_3$], respectively. This basic conclusion was confirmed by Farkas *et al.* in their studies of the synthesis of pyrethroid acids.[7b] In contrast, Klimova and Arbuzov [8] proposed only ene adduct type structures for the products from the $AlCl_3$- or $SnCl_4$-catalysed addition of chloral to 2-methylpropene, 2-methylpent-1-ene, and cyclohexene. We have shown previously [9] that the Russian group incorrectly assigned the structure of the cyclic ether product derived from the cyclohexene adduct, and the present results indicate that the chloral–olefin–Lewis acid system affords products of greater subtlety and variety than was thought hitherto.

Choice of Catalyst and Reaction Conditions.—Much of the earlier work had been conducted under relatively forcing reaction conditions (≥10 mol% Lewis acid). Our initial investigations were based on the reaction of chloral with (−)-β-pinene for two main reasons: (*a*) the pinyl skeleton is sensitive to both carbonium ion and to free radical processes, being readily rearranged or cleaved to the bornyl or limonyl systems; (*b*) the *thermal* ene addition had been reported to occur under relatively mild conditions (90 °C/6 h) to give the adduct (1a).[10a]



In our hands the thermal reaction also gave small quantities of the radical-derived limonyl product (2a),[10a] even in the absence of peroxides, which co-distilled with the ene adduct (1a). The similar reaction of bromal afforded much tarry material, but the ene adduct (1b) could be obtained by heating the reactants in a sealed tube in the dark (46 °C/8 days). Reaction in boiling (40—60 °C) light petroleum (12 days) under normal laboratory lighting, however, afforded only the radical product (2b). Attempts to shorten the reaction time by employing radical initiators, or by irradiation with visible or u.v. light gave (2b) and much tar.

A range of high quality commercially available Lewis acids were examined for their effectiveness in promoting formation of the adduct (1a). Typical results are summarized in Table 1. With the solid Lewis acids (*e.g.* $AlCl_3$ or $FeCl_3$) catalysis was observed only if the catalyst dissolved, presumably by complexation of the Lewis base chloral. The usual order of addition of the reagents adopted was therefore solvent (if any), chloral, then Lewis acid, and finally the olefin. An immediate temperature rise on addition of the first few drops of the olefin generally signalled a successful reaction; this rise was less pronounced with olefins of much lower reactivity than (−)-β-pinene. External cooling was then normally applied, and the remainder of the olefin (1 equiv.) added fairly rapidly with the

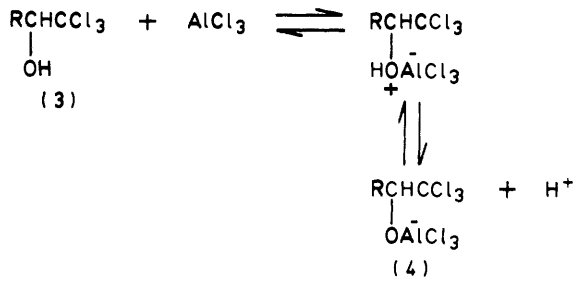
Table 1. The effect of catalyst and conditions on the ene addition of chloral to β-pinene at room temperature

Run	Catalyst	Mol%	Solvent [a]	Time (h)	Yield (1a) (%) [b]
1	$AlCl_3$	1	—	Too fast	Tar
2	$SnCl_4$	1	—	Too fast	Tar
3	$FeCl_3$	1	—	<1	62
4	$ZnBr_2$	4	—	1	14
5	$AlCl_3$	1	CCl_4	2	58
6	$AlCl_3$	2	CCl_4	1	61
7	$AlCl_3$	10	CCl_4	0.1	38
8	$AlCl_3$	20	CCl_4	<0.1	Tar
9	$SnCl_4$	2	CCl_4	1	59
10	$TiCl_4$	2	CCl_4	3	60
11	$FeCl_3$	2	CCl_4	5	59
12	$BF_3{\cdot}OEt_2$	2	CCl_4	24	27
13	$BF_3{\cdot}OEt_2$	5	CCl_4	8	56
14	BCl_3	*ca.* 5	CCl_4	24	*ca.* 5
15	Et_2ClAl [c]	100	CH_2Cl_2 $n\text{-}C_6H_{14}$	1	50

[a] Reactions are somewnat faster in CH_2Cl_2. [b] Yields are of purified (1a). [c] Catalyst in n-hexane added slowly to a CH_2Cl_2 solution of β-pinene and chloral.

temperature controlled to *ca.* 20—25 °C. Charge-transfer complexes may be formed for the reaction was also characterised by the development and fading of a yellow colour. The colour produced depended somewhat upon the olefinic substrate, and with less reactive olefins a non-fading reddish brown colour was frequently observed. Reaction times roughly parallel Lewis acidity (Table 1), and in the case of the more powerful Lewis acids it was necessary to *moderate* the reaction by utilising a solvent such as CCl_4 or CH_2Cl_2 (*cf.* runs 1—3 and 5, 6, 9, and 11). Solvents that are stronger Lewis bases than chloral towards, for example, $AlCl_3$ inhibit the reaction; these include ether, acetone, ethyl acetate, tetrahydrofuran, 1,2-dimethoxyethane, and nitrobenzene.The low activity of $BF_3{\cdot}OEt_2$ (runs 12, 13) may be due to such an effect. Although reaction rate was increased at higher concentrations of the Lewis acid (compare runs 5, 6, 7, and 8 and runs 12 and 13), this is counter-productive for an acid-sensitive olefin such as β-pinene. Even with the proton-scavenging Lewis acid Et_2AlCl, polymer formation with β-pinene was an important problem in the normal addition mode because of the necessity for 1 equiv. of the catalyst; also, appreciable reduction of chloral to 2,2,2-trichloroethanol occurred. With inverse addition, however, acceptable yields of (1a) were obtained (run 15). Product quality, on the whole, was better from the catalysed than from the thermal ene addition reactions.

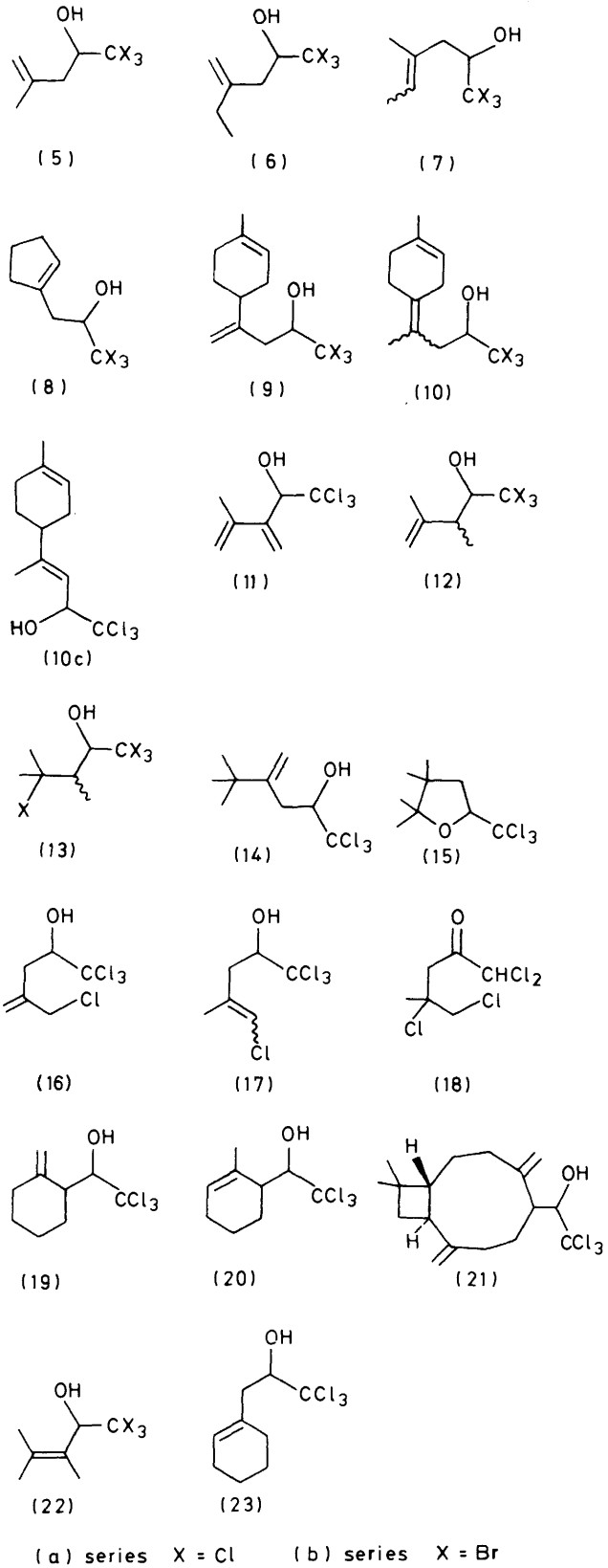
These model reactions showed the conditions of run 6 to be particularly convenient, and they were adopted as the standard reaction conditions for the greater part of this work. Use of CH_2Cl_2 as solvent is sometimes preferable, particularly with less reactive olefins, since reactions were noticeably faster than in CCl_4; the solvent can be dispensed with altogether for reactions involving liquid olefins of low reactivity (*e.g.* cyclohexene). Little improvement in yield resulted from the use of an excess of olefin, or of excess of chloral (work-up complicated through formation of chloral hydrate), or of further additions of $AlCl_3$ (slow rate of solution). It is probable that some chloral is lost to the reaction through hemiacetal formation with the ene adduct under $AlCl_3$ catalysis, and that catalyst loss occurs through processes such as (3) ⇌ (4). Additionally, pyrolysis of high boiling ene adducts such as (1a) occurs in purification through distillation under reduced pressure, and short path-length apparatus was employed in most cases.



Reactions of 1,1-*Dialkyl- and Trialkyl-ethylenes.*—Disubstituted terminal olefins are reported [1] to be the most reactive enes in conventional (thermal) ene reactions. They were also the most reactive group towards both chloral and bromal under the above standard $AlCl_3$-catalysed conditions. Typical results are summarised in Table 2. Trialkylethylenes, although somewhat less reactive, are also considered here as they behave very similarly.

The ^1H n.m.r. spectra obtained for the main products leaves no doubt that they are indeed ene adducts and not compounds resulting from Friedel-Crafts substitution. Thus, after exchange with D_2O the expected coupling pattern for the ABX spin system in the units $CH_2CH(OD)CX_2$ was revealed. We have also determined the structure of one of the diastereoisomers of (1a)-tosylate [11] and crystalline derivatives of other olefin–chloral adducts [5a] by *X*-ray methods, confirming the predominant formation of 1,1,1-trihalogenoalk-4-en-2-ols.

In the belief that Colonge and Perrot's [6] results may have arisen through the use of substantially more $AlCl_3$, or lower grade material, than used in the present study, we investigated various other reaction conditions (including the co-addition of dry HCl). In no case were the reactions deflected to give mainly Friedel-Crafts products. However, in the reaction of chloral with 2-methylbut-2-ene in the presence of 10 mol% $AlCl_3$ a non-ene product was observed (run 26a). Originally this compound was thought to be the Friedel-Crafts product but spectroscopic and analytical data indicate it to be the hydrochlorinated ene adduct (13a). A similar conclusion applies to the reaction involving bromal (run 27). Monitoring the standard chloral reaction (run 26) by capillary column g.l.c. revealed that at short contact times and at very low



conversions compounds (6a) and (7a) predominated although their actual yields were very low. These products are artefacts arising from a trace impurity of the more reactive olefin 2-methylbut-1-ene in the 2-methylbut-2-ene employed. On completion of the reaction (6a) and (7a) were scarcely detectable by ^{1}H n.m.r. in the presence of the main product (12a) which was formed more slowly. G.l.c. monitoring could be employed in a number of other reactions, and we found no evidence for the preliminary formation and prototropic isomerisation of Friedel-Crafts products. Instead, isomerisation of some of the ene adducts themselves occurred upon prolonged contact with the Lewis acid, especially in the reactions of the less reactive enophile bromal where longer reaction times were necessary. Additionally, storage of *purified* (6b) over a *long* period of time resulted in partial isomerisation into (7b), and (5b) was similarly isomerised into 1,1,1-tribromo-4-methylpent-3-en-2-ol, the Friedel-Crafts product. The *minor* by-product (10c) of the limonene–chloral reaction probably does not arise from the terminal olefinic ene adduct (9a) but is formed directly in a Friedel-Crafts type reaction (see Experimental section). Product structures were incorrectly assigned by Colonge and Perrot, therefore, in part as a result of the misinterpretation of chemical degradative hydrolysis results.[5b]

The results in Table 2 show that the ene reactions are completely regiospecific in the sense that only Markownikov-type addition was observed. There is a lack of regioselectivity (runs 19, 20, 23, 24, and 29) and this is discussed further in the following paper.[5a] The addition of chloral to 1-methylcyclohexene, however, appears to be highly regioselective. A minor g.l.c. peak of run 30 (<5%) is tentatively assigned to adduct (19). Prototropic rearrangement of (19) to (20) appears to be ruled out by the results obtained with the proton-scavenging Lewis acid Me_2AlCl (run 32). Appreciable reaction occurred between chloral and this catalyst or Et_2AlCl (run 31); in the latter case conversion into adducts was very poor and allowed the identification of (23) by ^{1}H n.m.r. Adduct (23) results from the presence of a trace impurity of methylenecyclohexane in the 1-methylcyclohexene sample, the exocyclic olefin being a highly reactive ene.

Our work confirms the report [10b] that α-pinene adds chloral in the presence of $AlCl_3$ to give cyclic ethers possessing the bornyl skeleton. The hindered olefin 2,3,3-trimethylbut-1-ene reacted with chloral (run 28) to give both the ene adduct (14) and the rearranged ether (15). Other instances of rearrangement processes are given in the following paper.[5a] The behaviour of 2-methylallyl chloride was somewhat intermediate between the olefins in this section and the alk-1-enes of the next section.

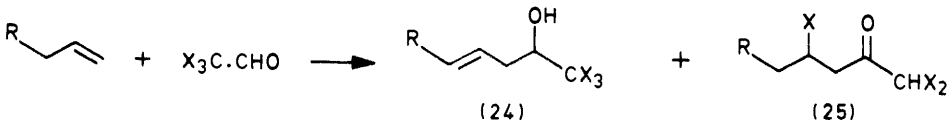
Reactions of Alk-1-enes.—These olefins were found to be less reactive than most of the alkenes in the previous section. The standard reaction conditions sufficed in most cases if at the expense of a modest increase in reaction time. Typical results are summarized in Table 3. The ene adducts (24) were predominantly the *E*-isomers shown.[5a] Ketonic compounds of structure (25) were formed in almost all of the reactions, and the two products invariably co-distilled under reduced pressure. The ketones are labile to base, and even pressure column chromatography over t.l.c. grade silica gel led to appreciable dehydrohalogenation to give the conjugated enone. The enone, for example (26) from (25d), was obtained more conveniently by treatment of the crude product mixture with pyridine followed by separation from the ene adduct (24d) by chromatography. The ketones (25) were isolated in a number of cases by chromatography on 100—200 mesh silica gel (*not* Brockmann I activity) using gravity flow to effect separation from the ene adduct (24). Additionally, (24b) and (25b) were separated, with isolation of (25b), by small-scale preparative g.l.c. on an analytical column (run 35). In order to separate the two components (24) and (25) in the mixtures of products, it was generally more convenient to convert ketones (25) into the corresponding enones by treatment with base followed by chromatography. For the isolation of the ene adduct alone,

Table 2. Aluminium chloride catalysed ene additions of chloral and bromal to 1,1-di- and 1,1,2-tri-alkylethylenes

Run	Alkene	Enophile [a]	Product [ratio]	Mol% $AlCl_3$	Time (h)	Yield (%) [b]
6	(−)-β-Pinene	C	(1a)	2	1	58
16		B	(1b)	2	6	65
17	2-Methylpropene	C	(5a)	2	2	55
18		B	(5b)	2	5	64
19	2-Methylbut-1-ene	C	(6a) + (7a) [47 : 53] [e]	2	2	49
20		B	(6b) + (7b) [25 : 75] [e]	2	24	43
21	Methylenecyclopentane	C	(8a)	2	2	79
22		B	(8b)	2	4	48
23	(+)-Limonene	C	(9a) + (10a) + (10c) [79 : 15 : 6]	2	2	41
24		B	(9b) + other products	6	24	20
25	3-Methylbuta-1,2-diene	C	(11) + other products	2	3	14
26	2-Methylbut-2-ene	C	(12a)	2	4	55
26a		C	(12a) + (13a) [55 : 45]	10	4	55
27		B	(12b) + (13b) [75 : 25]	2	18	25
28	2,3,3-Trimethylbut-1-ene	C	(14) + (15) [67 : 33]	2	3	61
29	Methylallyl chloride	C	(16) + *E*-(17) + *Z*-(17) + (18) [9 : 2.3 : 1.4 : 1] [e]	2	7	77
30	1-Methylcyclohexene	C	(19) + (20) [<5 : 95]	6	24	52
31		C	(20) + (23) [67 : 33]	100 [c]	24	10
32		C	(19) + (20) [~2 : 98]	100 [d]	3	35
33	β-Caryophyllene	C	(21) + other products	5	4	10

[a] C = Chloral, B = bromal. [b] Combined yields of all *isolated* products. [c] Et_2AlCl as catalyst; reduction of chloral to 2,2,2-trichloroethanol occurred. [d] Me_2AlCl as catalyst; Me addition to chloral also gave 1,1,1-trichloropropan-2-ol. [e] Mixture of products which could not be separated.

Table 3. Aluminium chloride catalysed ene additions of chloral and bromal to alk-1-enes

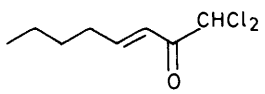


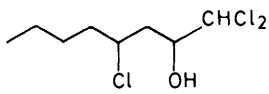
Run	Olefin (R)	Products (24) : (25)	Enophile X	Mol% $AlCl_3$	Time (h)	Yield (%) [a]
34	H	(a) 1 : 1	Cl	2	2—4	80
35		(b) 1 : 6	Br	2	4	73
36	CH_3	(c) 5 : 4	Br	2	6	54
37	n-C_3H_7	(d) 7 : 3	Cl	2	2—4	80
38		(e) 5 : 3.5	Br	2	4	68
39	n-C_4H_9	(f) 3 : 2	Br	2	4	80
40	n-C_5H_{11}	(g) 7 : 3	Cl	2	2—4	80
41		(h) 3 : 2	Br	2	4	83
42	$H_2C{=}CH(CH_2)_3$	(i) 5 : 2 [b]	Cl	2	3	44
43		3 : 5 [c]	Cl	2	18	55
44	C_6H_5	(j) 3 : 6 : 4 [d]	Cl	5	1	50
45		0 : 6 : 7 [d]	Cl	10	1	65
46		16 : 11 : 0 [e]	Cl	100 [f]	1.5	55
47	Br	(k) *ca.* 0 : 100	Cl	10	6	85
48	$CH{=}CH(CH_2)_2$ | CH_2CO_2Et	(l) *ca.* 4 : 1	Cl	50	168	54

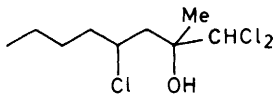
[a] Combined yields of all *isolated* products. [b] Five-fold excess of olefin employed using inverse addition. [c] Five-fold excess of chloral employed using normal addition; ratio refers to compounds (34) : (35) which were isolated after acetylation. [d] Ratio refers to compounds (24j) : (25j) : (31). [e] Ratio refers to compounds (24j) : (25j) + (33) : (31). [f] Me_2AlCl in n-hexane as catalyst; competing Me addition to chloral also gave 1,1,1-trichloropropan-2-ol.

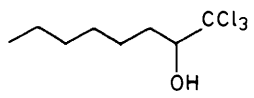
however, it was simpler to destroy the ketone by reaction with magnesium in boiling diethyl ether. The product ratios given in Table 3 were determined from ^1H n.m.r. integrals; g.l.c. analysis with f.i.d. detection is probably not reliable because polyhalogen compounds have low response factors through the operation of electron capture effects, which are likely to differ for alcohols and ketones. Only the lower molecular-weight adducts chromatograph without appreciable decomposition on conventional packed g.l.c. columns.

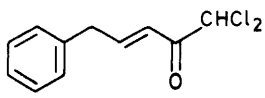
The amount of ketonic product is at a maximum with propene (run 34), but ascent of the homologous olefin series in the chloral reactions (runs 37, 40) resulted in the ene addition becoming the predominant process with the (24) : (25) ratio assuming a fairly constant 70 : 30 value. A similar trend was

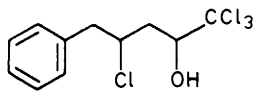

(26)

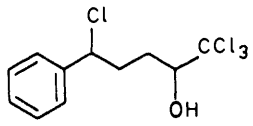

(27)

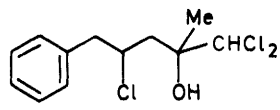

(28)

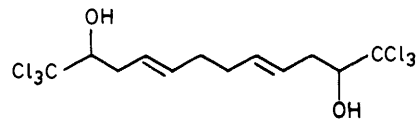

(29)


(30)


(31)


(32)


(33)


(34)

observed in the bromal reactions, but with a greater bias towards the ketones (25). The addition of chloral to hex-1-ene in CH_2Cl_2 solution was examined in some detail to optimise the yield of (24d). A number of Lewis acids [*e.g.* $SiCl_4$, $ZnCl_2$, $HgCl_2$, $Hg(OAc)_2$, and 14% $AlCl_3$–graphite intercalate] were found to be ineffective catalysts. Only the more powerful Lewis acids (*e.g.* $AlCl_3$, $SnCl_4$, $SnCl_4 \cdot 5H_2O$, $FeCl_3$, $TiCl_4$, and $AlCl_3 \cdot NaCl \cdot KCl$ eutectic) promoted the reaction, but the 70 : 30 ratio of (24d) : (25d) deteriorated to 61—64 : 39—36 on replacement of $AlCl_3$ by these other catalysts. The co-addition of dry HCl to the $AlCl_3$-catalysed reaction likewise led to a marginal increase in ketone formation (63 : 37). The most advantageous product balance (90 : 10) was obtained with Brockmann I silica gel as a heterogeneous catalyst and hexane as solvent; reaction, however, was extremely slow. The proton-scavenging dialkylaluminium chlorides (100 mol%) were also employed. With Et_2AlCl rapid reduction of (25d) occurred to give the alcohol (27), a 43 : 57 mixture of diastereoisomers. Because the catalyst also reduced chloral, the best results were obtained by adding the Et_2AlCl in hexane dropwise to a 1 : 1 mixture of reactants in CH_2Cl_2 and afforded a 63 : 37 ratio of (24d) : (27) in 40% yield. In the case of catalysis by Me_2AlCl the alternative complication of methyl addition to chloral and (25d), giving 1,1,1-trichloropropan-2-ol and a 50 : 50 mixture of the diastereoisomeric alcohols (28), was observed. The methyl addition from Me_2AlCl is a slower process than H-transfer from Et_2AlCl since traces of (25d) survived the reaction conditions. Some variation in the ratio of products (24d) : (25d) + (28) was observed depending upon the order of addition of reagents, but the bias towards the ene adduct (24d) was gained only at the expense of a lower combined yield. Thus, addition first of chloral and then of hex-1-ene to Me_2AlCl in hexane gave an 84.5 : 15.5 mixture (30%). On balance, therefore, the standard conditions using $AlCl_3$ are generally to be preferred.

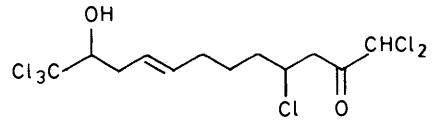
Substituents other than alkyl at the allylic centre of propene had the effect of markedly reducing reactivity towards chloral, and higher $AlCl_3$ concentrations were necessary to promote reaction at a reasonable rate (runs 44—47). The fall in olefin reactivity was also marked by an increase in ketone formation, and with allyl bromide (run 47) the normal ene addition could no longer be detected. Bromal and allyl bromide, and chloral with either allyl cyanide or methyl vinylacetate failed to react. Allyl alcohol merely afforded trichloroacetaldehyde allyl hemiacetal; the employment of Et_2AlCl (200 mol%) resulted in the precipitation of aluminium alkoxides.

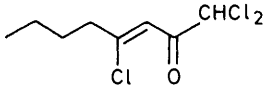
Allylbenzene reacted with chloral to give (24j), (25j), and (31); chromatographic isolation of (25j) resulted in its partial dehydrochlorination to (30). Fortunately (31) was crystalline, which enabled its isolation and purification; it was converted cleanly and in good yield into (24j) on treatment with DBN. Clearly (31) is not the result of HCl addition to the ene adduct (24j), for mechanistic considerations indicate that such reaction should give (32). Hence, the genesis of (13a) was also open to question. A number of experiments were conducted in attempting to discover the source of (31) (*e.g.* runs 45, 46). From a number of $AlCl_3$-catalysed reactions it was found that whereas the ratio (25j) : (24j) + (31) was more or less independent of the $AlCl_3$ concentration, the ratio (24j) : (31) depended upon the quantity of Lewis acid. This indicates a close mechanistic link between (24j) and (31). The absence of (31) in run 46 could be due to the absence of HCl through the proton scavenging action of Me_2AlCl; however, there is also a reduced availability of Al–Cl species. It seems likely, therefore, that (31) is formed directly from chloral and allylbenzene by way of a Friedel-Crafts intermediate–Lewis acid complex. Chloride transfer from the $AlCl_3$ moiety to the carbocationic centre would afford (31) exclusively.[5a]

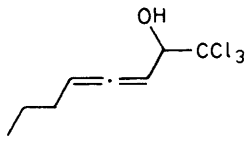
The results of the addition of chloral to hex-1-yne were of particular interest in the above connection. Because of the lower reactivity of alk-1-ynes relative to alk-1-enes,[1] the need for 6 mol % $AlCl_3$ was not surprising. Capillary column g.l.c. indicated the formation of five products, the peak area ratios in order of elution being 5 : 23 : 22.5 : 6 : 43.5. Chromatographic isolation allowed the positive identification of peaks 1, 2, 3, and 5, respectively as ketone (36), ene adduct (37) (both diastereoisomers), and hydrochlorinated compound (38). The structure of (38) serves to emphasise the invariable α,γ substitution pattern of OH and Cl groups in the hydrochlorinated adducts, a feature entirely consistent with the mechanism involving Cl transfer from complexed $AlCl_3$.[2,5a] On the other hand, addition of HCl to (37), an internal allene, should be non-regiospecific and afford four adducts.

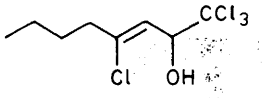
The effects of remote functional groups on the reactivity of terminal alkenes was studied briefly (runs 42, 43, and 48). The results for octa-1,7-diene (runs 42, 43) were unexceptional, the second double bond merely providing an additional site for reaction. The ester function of ethyl nona-3,8-dienoate (run 48) retarded reaction as a result of competition with chloral for complexing $AlCl_3$. Hence, even with 50 mol% $AlCl_3$ the reaction time for reasonable conversion to products was rather long.

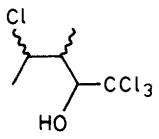
Reactions of 1,2-*Dialkylethylenes.*—Generally speaking, only the most reactive enophiles afford ene adducts with 1,2-dialkylethylenes; [1] the results obtained are summarized in Table 4, and are testimony to the relatively high reactivity of the $Cl_3C \cdot CHO$—$AlCl_3$ system. The thermal additions to these olefins (and to the more reactive alk-1-enes) failed. The need for relatively high $AlCl_3$ concentrations led to significant polymer formation with simple acyclic olefins (runs 49—52). *cis*-But-2-ene was distinctly more reactive towards chloral than was *trans*-but-2-ene. The *cis*-olefin afforded a mixture of

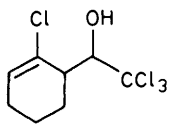

(35)

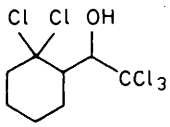

(36)

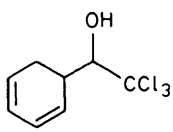

(37)

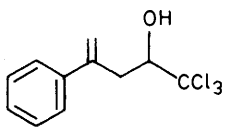

(38)


(41)


(42)

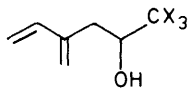

(43)

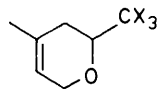

(44)


(45)

the ene adduct (39a), as a *ca.* 3 : 1 mixture of diastereoisomers, and the ketone (40a). In contrast, *trans*-but-2-ene gave mainly ketone (40a) and hydrochlorinated compound (41). This result argues particularly strongly against the scheme (ene adduct) + (HCl) ⟶ (hydrochlorinated adduct), but is consistent with the intramolecular delivery of chloride from complexed $AlCl_3$ in a Friedel-Crafts type intermediate. The differences in the products arises from differences in topology of the ene/enophile interactions.[5a]

Simple cycloalkenes reacted smoothly with chloral to give ene adduct (39) and ketone (40), the ketone forming process being much more prominent with cycloheptene. The ene adducts rearranged on prolonged contact with $AlCl_3$ to give cyclic ethers, and we have shown that (39c) is transformed into 7-trichloromethyl-6-oxabicyclo[3.2.1]octane.[9] It seems likely, therefore, that the other chloral–cycloalkene ene adducts are similarly rearranged to (*n* + 3)-oxabicyclo[*n*.2.1]alkanes. Cyclic ether formation was found to be unavoidable in the bromal additions because of the need for high $AlCl_3$ concentrations (runs 55, 57, and 59). In the chloral additions the loss of ene adduct can be minimised by shortening the contact time by dispensing with the solvent (*e.g.* run 54). The ene adducts (39b, c, e, and g) could be purified simply, as before, by selectively decomposing the corresponding ketones (40) by reaction with magnesium. There is an interesting variation in the (39) : (40) ratio with ring size for the chloral reactions. Molecular models suggest a congested transition state for ene addition to cycloheptene (run 56), and the adduct itself was particularly prone to conversion into the cyclic ether. In comparison with cyclohexene, 1-chlorocyclohexene was found


(46) a ; X = Cl
b ; X = Br


(47) a ; X = Cl
b ; X = Br

to be only weakly reactive (5 mol% $AlCl_3$, 24 h). Reaction afforded a 2 : 1 mixture of ene adduct (42) and another chloro-alcohol which is believed to be the hydrochlorinated product (43). No evidence was obtained for the formation of a ketonic product. It appears, therefore, that ketone formation requires that the olefinic substrate be only moderately reactive and that it should not possess two substituents at one C=C terminus.

Only polymeric products were observed in the chloral–cyclopentadiene reaction (run 61). Cyclohexa-1,4-diene reacted with chloral to give benzene and 2,2,2-trichloroethanol (run 60); ene addition to give (44) followed by elimination is the probable reaction pathway. The reactions of chloral with cyclohexa-1,3-diene have been discussed elsewhere.[9]

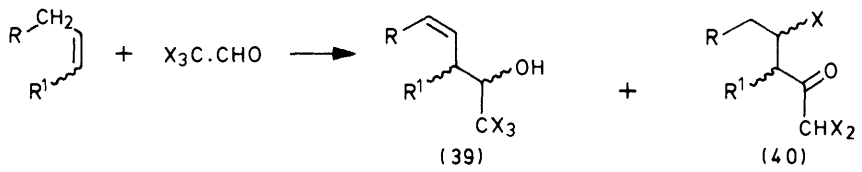
Reactions of 2-Substituted Propenes.—The Lewis acid catalysed reactions of chloral with a number of 2-substituted propenes, $CH_3C(Y)=CH_2$, were examined to determine those stereoelectronic effects that are beneficial towards the ene addition.

(a) *α-Methylstyrene.* This was of similar reactivity to 1,1-dialkylethylenes and gave only ene adduct (45) under the standard reaction conditions. Although some olefin polymerisation was observed, (45) did not suffer prototropic rearrangement. Similar reaction of *p*-methoxy-α-methylstyrene appeared to afford products only of electrophilic aromatic substitution and polymerisation.

(b) *Isoprene.* This may be also be classified as a reactive ene of the 1,1-dialkylethylene type. Reaction with both chloral and bromal afforded only the ene adduct (46) and the formal Diels–Alder adduct (47). The chloral addition reaction was studied in some detail, and it was found that the (46a) : (47a) ratio depended upon reaction conditions and duplicate experiments suffered from poor reproducibility. The ene adduct (46a) was favoured by a low $AlCl_3$ concentration and a short contact time, which indicated that much of the Diels–Alder product was derived from (46a) in a secondary reaction. Treatment of (46a) in CCl_4 in an n.m.r. tube with 5 mol% $AlCl_3$ led to its complete conversion into (47a) in 2 h at room temperature; the reaction was monitored by observing particularly the change in the olefinic ^1H n.m.r. resonances. A possible mechanism is outlined in Scheme 1 which relies upon the presence of catalytic quantities of a protonic acid impurity, formed *via* (3) ⇌ (4). Protonic acid is absent in the 100 mol% Et_2AlCl catalysed addition,[2] and reaction at −30 °C (to minimise olefin polymerisation) gave a 30% yield of a 3 : 1 mixture of (46a) and (47a) after 20 min. This bias in favour of the ene adduct corresponded to about the best that could be achieved with $AlCl_3$ (1 mol%, 2—4 h). G.l.c. assay of the product mixtures from the $AlCl_3$-catalysed reactions gave the following approximate (46a) : (47a) ratios: 1.2 : 1 with 2 mol% for 1 h, 0.4 : 1 with 5 mol% for 15 min, and 0.02 : 1 with 10 mol% for 5—10 min. The thermal addition is reported to give a 0.11 : 1 product mixture at 145 °C (20 h).[1,8]

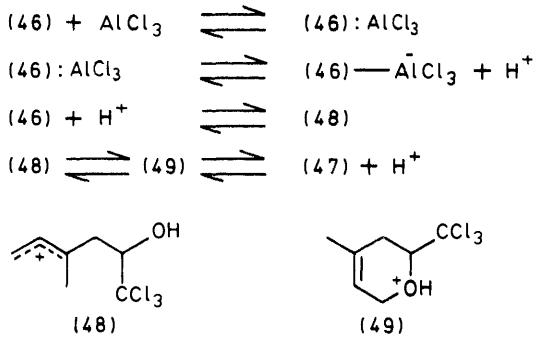
(c) *Isopropenyl acetate.* This reacted with chloral in the presence of 5—20 mol% $AlCl_3$ to give four products (50)—(53) whose ratio depended upon the catalyst concentration and reaction time; typical results are summarized in Table 5. The favoured product, even for the thermal addition, was (50) which could be regarded as resulting from an 'acyl ene'

Table 4. Aluminium chloride catalysed ene additions of chloral and bromal to 1,2-dialkylethylenes



Run	Olefin R,R¹	Products (39) : (40)	Enophile X	Mol% $AlCl_3$	Time (h)	Yield (%) [a]
49	*E*-(H,CH_3) [b]	(a) *ca.* 2 : 73 : 25 [c]	Cl	6	3	64
50		—	Br	6—20	12	Polymer
51	*Z*-(H,CH_3) [d]	(a) *ca.* 3 : 2	Cl	6	3	79
52		—	Br	6—20	12	Polymer
53	$-(CH_2)_2-$	(b) 95 : 5	Cl	6	3	44
54	$-(CH_2)_3-$	(c) 88 : 12	Cl	10 [e]	2	62
55		(d) 1 : 4 [f]	Br	20	24	36
56	$-(CH_2)_4-$	(e) *ca.* 2 : 3	Cl	6	2	65
57		(f) *ca.* 1 : 1 : 1 [g]	Br	20	24	24
58	$-(CH_2)_5-$	(g) 95 : 5	Cl	6	4	75
59		(h) *ca.* 1 : 1 [h]	Br	20	24	43
60	$-CH=CH-CH_2-$ [i]	—	Cl	2	3	— [i]
61	$-CH=CH-$	—	Cl	1—3	4	Polymer [j]

[a] Combined yields of all *isolated* products. [b] *trans*-But-2-ene. [c] Ratio refers to (39a) : (40a) : (41). [d] *cis*-But-2-ene. [e] Reaction conducted without solvent. [f] Ratio refers to (39d) : (cyclic ether); see text and Experimental section. [g] Ratio refers to (39f) : (40f) : (cyclic ether); see text and Experimental section. [h] Ratio refers to (39h) : (cyclic ether); see text and Experimental section. [i] Cyclohexa-1,4-diene; only benzene and 2,2,2-trichloroethanol were detected as reaction products; see text. [j] Polymer formation occurred even at −75 °C.



Scheme 1.

Table 5. Product yields from the aluminium chloride catalysed addition of chloral to isopropenyl acetate

Mol% $AlCl_3$ [a]	(50)	(51)	(52)	(53)	Total yield (%) [b]
5	10	3	6	—	10
10	8	4	5	—	45
20	5	3	1	1	60
— [c]	3	1	—	1	11

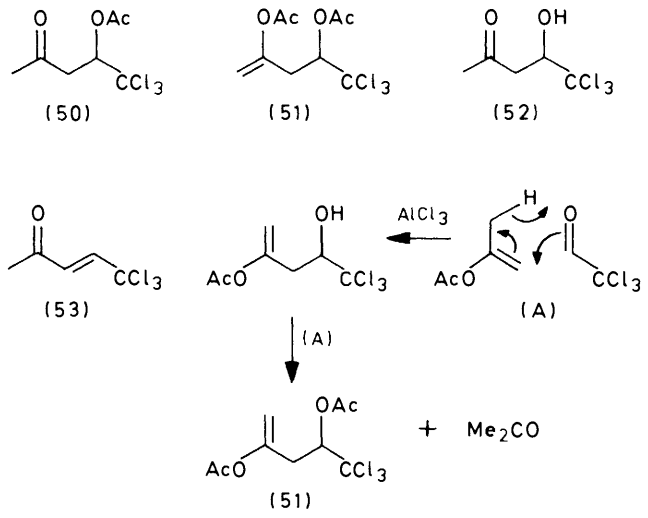
[a] 96 h for catalysed reactions. [b] Yields are for *isolated* products. [c] 140 °C, 24 h, tube sealed *in vacuo*.

reaction. Although such processes have been documented,[12a] a stepwise mechanism involving a modified aldol condensation appears to be more likely in the present case. The bis-acetoxy compound (51) presumably results from ene addition and subsequent acylation (Scheme 2). Control experiments indicated that no direct conversion of (50) into (51) occurred under the reaction conditions. The enone (53) is believed to arise from the elimination of acetic acid from (50) rather than from dehydration of (52). The formation of (52) only in the presence of $AlCl_3$ can be rationalized as in Scheme 3. Interestingly, we were unable to promote direct condensation of chloral with acetone under our conditions of $AlCl_3$ catalysis.

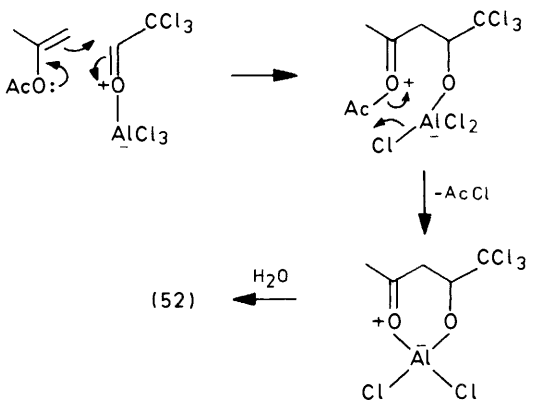
(d) *Isopropenyl methyl ether.* This reacted with chloral in the presence of 2—10 mol% $AlCl_3$, but only the hemiacetal (54) could be isolated. This product is presumably formed only as a consequence of the hydrolytic work-up in which the methanol thus generated added to the chloral. The thermal reaction (120 °C/24 h, sealed tube) afforded a mixture of products (55%) of which the five major components were (54)—(57) and (52) in the ratio *ca.* 4 : 4 : 2 : 2 : 3, respectively. Although it is possible that (52) could be derived from the ene adduct (58), an aldol type reaction (Scheme 4) seems equally probable. The mode of formation of the pyranone (55) is not clear; a feasible mechanism, based on the ene adduct (58), is shown in Scheme 5. Alternatively, (55) may be derived from (52) through a similar series of reactions. The cyclisation step could involve the enol of the ketone or its enol ether (59). The genesis of the chlorine atom rearrangement products (56) and (57) is obscure. However, it is unlikely that either product is derived from (53) for the reason that no (53) could be detected, and the presence of (53) in the isopropenyl acetate–chloral reaction did not result in the formation of (56) or (57).[12b]

The reaction of 2-methoxypropene with chloral in the presence of 100 mol% Et_2AlCl was extremely vigorous, and even at −30 °C (2 h) a complex product mixture was obtained. The two major products, isolated by pressure column chromatography, were (55) and the 2 : 1 adduct (60); the latter compound possibly arises from further ene addition of chloral to (58) and subsequent hydrolysis of the vinyl ether in the work-up.

(e) 2-*Bromopropene.* This reacted sluggishly with chloral in the presence of 2 mol% $AlCl_3$ (*cf.* 1-chlorocyclohexene) to give the crystalline ene adduct (61) in 29% yield. A second solid product of slightly higher R_F value was isolated in low yield



Scheme 2.



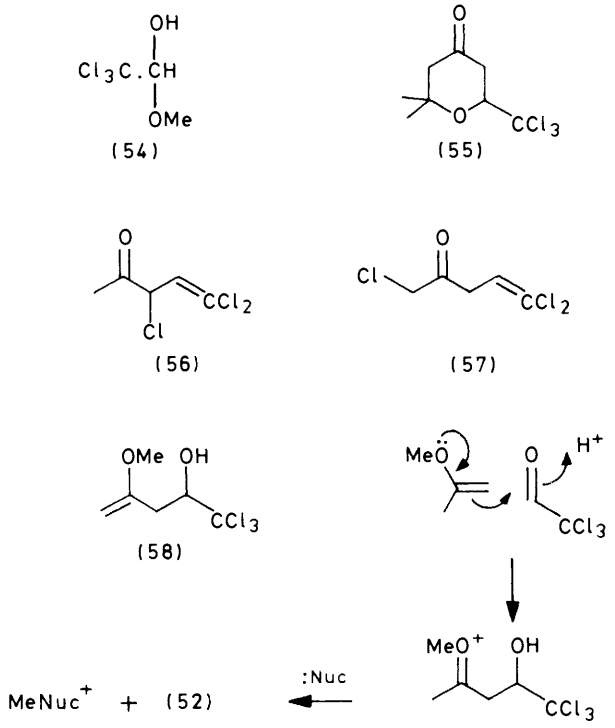
Scheme 3.

(5.5%) by column chromatography, and is assigned structure (62) on the basis of i.r. and ^{1}H n.m.r. evidence.

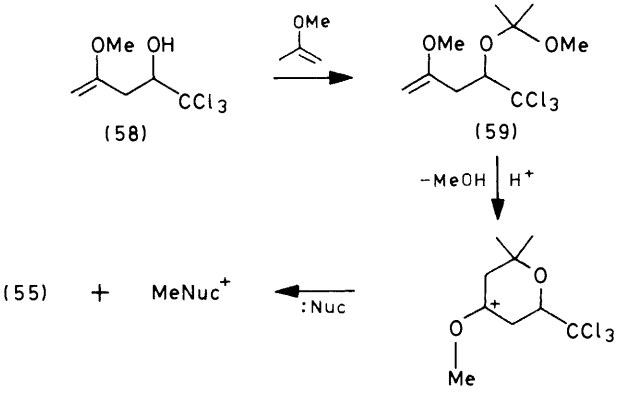
(f) *Methacrylonitrile and methyl methacrylate.* These failed to react with chloral, even in the presence of 20 mol% $AlCl_3$ for 96 h. It appears that olefins of this level of electronic deactivation undergo ene addition only with ' super-enophiles ' such as hexafluoroacetone or trifluoronitrosomethane.

General Conclusions.—The general trends in the results obtained indicate that the order of ene reactivity towards Cl_3CCHO–$AlCl_3$ falls approximately in the following series (where R = H, alkyl; R′,R″ = alkyl; V = vinyl, phenyl; X = halogen, OR etc.; Z = CO_2R, CN *etc.*): $RCH_2C(R')=CH_2 \sim RCH_2C(V)=CH_2 \geqslant RCH_2C(R')=CHR'' > RCH_2$-$CH=CH_2 > RCH(R')CH=CH_2 >$ *cis-* or *cyclo*-$RCH_2CH=CHR' > RCH_2C{\equiv}CH \geqslant$ *trans*-$RCH_2CH=CHR' \geqslant VCH_2$-$CH=CH_2 \sim RCH_2C(X)=CH_2 > XCH_2CH=CH_2 > RCH_2C$-$(Z)=CH_2 \sim ZCH_2CH=CH_2 \sim RCH_2CH=CHZ$.

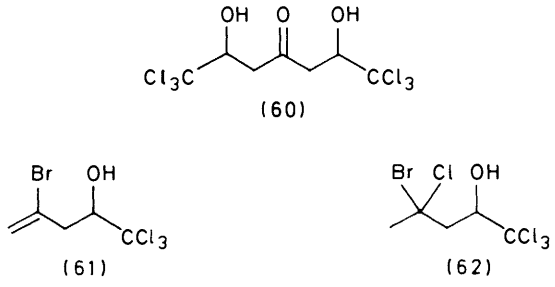
The bromal reactions fail after about the sixth member of each series, and with chloral >2 mol% $AlCl_3$ is necessary after the fifth member of each series. The thermal addition of chloral fails after the third member of each series. Ketonic by-products are formed in the catalysed chloral reactions with the fourth and subsequent members of the series except for compounds of the type $RCH_2C(X)=CH_2$; in this case acid-labile X functionality results in the formation of a variety of pro-



Scheme 4.



Scheme 5.



ducts. Hydrochlorinated ene adducts were observed in a number of reactions, particularly with the less reactive ' enes '. These compounds are difficult to detect for they possess similar R_F values on t.l.c. to the ene adducts themselves and stain very poorly with I_2 vapour or with $KMnO_4$; further, on g.l.c. they possess appreciably longer retention times than the ene adducts or ketonic products. Indeed, g.l.c. on packed

columns was successful only for the simpler adducts; analysis on glass capillary columns (which became available to us at the end of this study) was of wider applicability.

If the above reactivity trends can be translated to the general case enophile–Lewis acid, then the study of the reactions of relatively few olefins should give a fairly accurate picture of the reactivity of any given enophile–Lewis acid combination, within limits. In our continuing studies we employ the following ' reactivity series olefins ': [5a] β-pinene or methylenecyclohexane > hex-1-ene > cyclohexene > hex-1-yne. In all cases encountered thus far these initial limited studies have given a fairly accurate picture of the enophile–Lewis acid reactivity when a wide range of olefins was studied subsequently.

Experimental

Melting points were determined on a Kofler block, and are uncorrected. Optical rotations were measured in an ETL-NPL automatic polarimeter or an Optical Activity AA-10 automatic digital polarimeter using cells of 1 dm path length and chloroform as solvent; when sample concentrations are not given they were in the range 1.6—2.0 g/100 ml. Elemental analyses for C, H, and N were determined by a Perkin-Elmer model 240B instrument, and halogen was determined by the Schoniger oxygen flask method. Pressure column chromatography was performed on Fluka t.l.c. grade silica gel G containing 13% gypsum, and pressure was applied by a Hi-Flo Junior aquarium pump; 40 g of silica gel per g of substrate was generally employed. Analytical t.l.c. was carried out on 20 × 5 cm glass plates with *ca.* 1 mm thick layer of silica gel G or on Merck silica gel 60 F_{254} plates of 0.2 mm layer thickness on plastic backing. Separated components were visualized by exposure to iodine vapour or u.v. radiation; in some cases potassium permanganate spray was used. Analytical g.l.c. utilizing conventional packed columns was performed on a Perkin-Elmer 800 or Pye 104 instrument; high resolution capillary column g.l.c. was carried out on a Perkin-Elmer Sigma 2 instrument using 25 and 50 m glass capillary columns. In all cases the carrier gas was nitrogen.

Mass spectra were recorded with an AEI MS-902 mass spectrometer: g.l.c./m.s. analyses were performed on a VG Micromass 7070F spectrometer equipped with VG Data-system 2000 and connected to a Pye 104 g.l.c. *via* a jet separator. I.r. spectra were calibrated, and were recorded on a Unicam SP200 or Perkin-Elmer 710B spectrometer; u.v. spectra were measured in a Unicam SP800 spectrophotometer. Routine ^1H n.m.r. spectra were recorded in a Hitachi Perkin-Elmer R24A 60 MHz, Jeol JNM-MH-100 100 MHz, or Perkin-Elmer R32 90 MHz continuous wave spectrometer; highfield ^1H n.m.r. spectra were recorded in a Bruker WM 250 PFT spectrometer. Carbon-13 n.m.r. spectra were recorded either in a Jeol JNM-PS-100 PFT or the Bruker WM 250 PFT spectrometer. In all cases $CDCl_3$ was employed as solvent (unless stated otherwise), and chemical shifts (relative to internal $SiMe_4$) are quoted on the δ scale (p.p.m. downfield from $SiMe_4$).

Reagents.—Dichloromethane and carbon tetrachloride were dried over crushed anhydrous $CaCl_2$, filtered, and distilled through a Vigreux column; they were stored over type 4A molecular sieves. Hexane was distilled from lithium aluminium hydride.

Chloral and bromal were shaken with concentrated sulphuric acid (5 : 1, v/v), separated, and distilled through a Vigreux column at, respectively, atmospheric pressure and 2—20 mmHg. The enophiles were generally redistilled immediately before use. The metal halide Lewis acid catalysts employed were the high quality materials available from Fluka; they were used without further purification excepting $SnCl_4$ which was redistilled before use. Titanium tetrachloride was handled and dispensed under argon atmosphere to minimise fuming through hydrolysis by atmospheric moisture. Diethylaluminium chloride and trimethylaluminium were 25% (w/w) solutions in hexane as supplied by Alfa-Ventron. The bulk solutions were transferred under argon into a number of 50 ml ' Hypovials ' by using the double-ended needle technique. The vials were capped and sealed with either Teflon-faced silicone rubber septa or with ' Hycar ' septa (all items from Pierce); batches of vials were placed in a sealable can containing desiccant and flushed with argon, and stored at *ca.* 0 °C. The alkylaluminium reagents were dispensed by syringe; punctured septa were protected with ' Nescofilm ', and the contents of part-used vials did not noticeably deteriorate during several weeks. The contents of vials with unpunctured septa were unaffected after storage as above for longer then 12 months. In contrast, because of the ineffective seal (once punctured) of the original container, the bulk reagents deteriorated rapidly even when positive steps were taken to effect transfers under argon atmosphere only. Dimethylaluminium chloride was prepared from trimethylaluminium and aluminium chloride as detailed below.

Inexpensive olefins were distilled prior to use [from $LiAlH_4$ in the case of (+)-limonene]; expensive or gaseous olefins were used as supplied unless reaction failed, when the liquid olefins were dried ($MgSO_4$ or $CaCl_2$) and distilled and the gaseous olefins were passed over type 4A molecular sieves.

2-Methylbut-2-ene was prepared by the dehydration of 2-methylbutan-2-ol with 33% sulphuric acid; [13] 1-methylcyclohexene was prepared by the dehydration of 1-methylcyclohexanol (obtained from the Grignard reaction of methylmagnesium iodide with cyclohexanone) with oxalic acid; [14] 1-chlorocyclohexene was prepared by Braude and Coles' procedure [15] from cyclohexanone and PCl_5 by way of 1,1-dichlorocyclohexane.

General Procedures for Lewis Acid Catalysed Ene Reactions

(a) *Trihalogenoacetaldehyde Reactions using Conventional Catalysts.*—(1) *Liquid olefins.* Reactions were normally carried out on the 5—50 mmol scale with 2 mol% catalyst for reactive alkenes rising to 10 mol% for less reactive systems. The apparatus comprised a dry three-necked flask, containing a magnetic flea and fitted with a rubber septum in the centre neck, a combined nitrogen inlet and alcohol thermometer in the second neck, and a mineral oil bubbler to form a break to the atmosphere in the third neck. Typical experimental details are as follows.

To a stirred solution of the trihalogenoacetaldehyde (20 mmol) in dry CH_2Cl_2 (20 ml) and under an atmosphere of N_2, was added the anhydrous catalyst (0.4—2 mmol, 2—10 mol%). Solid catalysts were finely powdered before the addition. When dissolution of the catalyst was complete (*ca.* 2 min), the alkene (20 mmol) was added dropwise by means of a syringe through the septum. If an exothermic reaction was observed the solution, which normally became coloured, was cooled in a bath of iced water to maintain a temperature of 20—25 °C during the alkene addition; in this way the bulk of the alkene could be added fairly rapidly. After the mixture had been stirred at room temperature for the desired period of time, typically 1—4 h, but occasionally 1—2 days, the solution was diluted with ether (100 ml), washed with saturated aqueous sodium hydrogen carbonate (2 × 40 ml) and water (40 ml), and dried ($MgSO_4$ or Na_2SO_4). Filtration followed by removal of the solvent under reduced pressure afforded the crude product which was normally distilled under reduced pressure then, if

necessary, subjected to pressure column chromatography (solvents: CH_2Cl_2, $CHCl_3$, or C_6H_6 as appropriate). Following the chromatography the products, which were virtually all colourless oils, underwent final purification by Kugelröhr distillation.

All quoted yields are for isolated and purified products, unless specified otherwise. In most cases no attempt has been made to optimise product yields.

Note: Reactions utilizing $FeCl_3$ or $ZnBr_2$ as catalyst were conducted in the absence of solvent. Likewise, the solvent can be dispensed with when using $AlCl_3$ if the alkene is of the weakly reactive type (*e.g.* cyclohexene).

(2) *Gaseous olefins.* The procedure was as described for liquid olefins. After dissolution of the catalyst in the solution of the trihalogenoacetaldehyde the nitrogen inlet was replaced by a delivery tube with a sintered glass disc through which the gaseous olefin was introduced below the level of the solution in the flask. Excess of olefin was invariably used, and the flow rate was adjusted to maintain a slight positive pressure in the apparatus. In the case of the more readily condensed alkenes (*e.g.* the but-2-enes) the gas flow was interrupted, as necessary, to prevent the excessive build-up of the alkene in solution. Reaction times were as for the related liquid olefins, and cooling was necessary only for the first few minutes of the olefin delivery. The reaction mixture was stirred at room temperature for the required time, and then worked-up as above.

(b) *Preparation of Dimethylaluminium Chloride.*—The apparatus comprised a flame-dried three-necked flask containing a magnetic flea and fitted with a rubber septum in the centre neck, a gas inlet in the second neck, and a short condenser in the third neck. The top exit of the condenser was fitted with a mineral oil bubbler equipped with a stopcock so that it could be isolated from the condenser/flask assembly. The gas inlet was attached to a manifold *via* a two-way tap so that the flask could be alternately connected to the vacuum line or to the argon supply. The system was flushed with argon and finely powdered anhydrous aluminium chloride (0.467 g, 3.5 mmol) introduced into the flask. The flask was evacuated to 1 mmHg pressure, then filled with argon; this cycle was repeated and a steady stream of argon then passed through the reaction flask. The aluminium chloride was suspended in dry hexane or dichloromethane (4 ml) and a 25% (w/w) solution of trimethylaluminium in hexane (3.07 ml; 0.529 g Me_3Al, 7.33 mmol) was added dropwise with stirring. Transfer of the Me_3Al solution was effected by a Luer-lock syringe; the syringe was rinsed with dry hexane and argon before use to prevent contact of the reagent with the atmosphere. The $AlCl_3$ dissolved rapidly to give a clear colourless solution of Me_2AlCl which was used immediately.

The validity of this method of preparing Me_2AlCl rests on the finding,[16] based on ^1H n.m.r. evidence, that alkyl group transfer between R_3Al and $AlCl_3$ is very rapid in solution at room temperature and, depending upon stoicheiometry, the principal species at equilibrium is R_2AlCl or $RAlCl_2$. In the above procedure the use of an excess of Me_3Al over the theoretical 2 : 1 ratio was deliberate so that the formation of $MeAlCl_2$, a much stronger Lewis acid, was inhibited.

(c) *Chloral Reactions using Dialkylaluminium Chloride Catalysts.*—*Method* 1. To a stirred solution of anhydrous chloral (1.475 g, 10 mmol) and alkene (10 mmol) in dry hexane or dichloromethane (6 ml), under an atmosphere of argon and cooled to 10 °C in an ice-bath using the apparatus described in (b), was added dropwise by syringe either the freshly prepared solution of dimethylaluminium chloride (10 mmol), or a commercial 25% (w/w) solution of diethylaluminium chloride in hexane (6.58 ml; 1.21 g Et_2AlCl, 10 mmol). Reaction was normally highly exothermic and accompanied by vigorous evolution of gas (methane or ethane). The rate of catalyst addition was controlled so that the temperature did not exceed 25 °C. The solution was stirred at room temperature for 1—2 h, then cooled in ice and quenched by the very cautious addition of saturated aqueous sodium hydrogen carbonate solution (5 ml) whilst still maintaining the argon atmosphere. The precipitated alumina was removed by suction filtration and washed thoroughly with ether (50 ml). The filtrate was finally washed with water (15 ml) and dried ($MgSO_4$ or Na_2SO_4). Filtration and removal of the solvent under reduced pressure afforded the crude product which was distilled under reduced pressure or purified by pressure column chromatography and Kugelröhr distillation, as appropriate.

Method 2. To a freshly prepared solution of dimethylaluminium chloride (10 mmol) or a commercial 25% (w/w) solution of diethylaluminium chloride in hexane (6.58 ml; 1.21 g Et_2AlCl, 10 mmol), further diluted with hexane or dichloromethane (5 ml), cooled to 10 °C and under argon [apparatus as in (b)], was added dropwise by syringe, and with stirring, a mixture of anhydrous chloral (1.475 g, 10 mmol) and the alkene (10 mmol). When addition was complete the solution was stirred at room temperature for 1—2 h, prior to quenching and work-up as for Method 1.

General Procedure for Thermal Ene Reactions of Chloral

(a) *Reactions under Air.*—Equimolar quantities of anhydrous chloral and the alkene were placed in a small Carius tube together with a few milligrams of quinol to inhibit alkene polymerisation. The tube was fitted with a $CaCl_2$ guard tube by means of a sleeve connection, and the liquid contents frozen by immersion in liquid nitrogen; the tube was then immediately flame sealed, allowed to regain room temperature, and then placed in a cavity of an electrically heated metal block equipped with a thermocouple temperature control. After the desired reaction time the cooled tube was cut open, and the contents distilled under reduced pressure.

(b) *Reactions* in vacuo.—The trihalogenoacetaldehyde, alkene, and quinol inhibitor were placed in a small Carius tube equipped with a high vacuum Teflon screw valve (Young's valve) and side arm. The mixture was degassed by employing several freeze–thaw cycles and the tube was then sealed *in vacuo*, allowed to regain room temperature, and heated in the metal block as before. The work-up procedure was as given in (a).

Note: The air-sealed Carius tube was totally submerged in the heated cavity, whereas the Young's valve tube necessarily protruded *ca.* 4 cm above the cavity to ensure that undue softening of the Teflon valve did not occur. Consequently, the cooler portion of the vacuum-sealed tube acted as a condenser for the reflux of the chloral–alkene mixture.

Removal of Trihalogenoketone By-products from Ene Adducts by a Grignard-type Procedure.—The removal of 1,1,4-trichloro-octan-2-one (25d) from the ene adduct, 1,1,1-trichloro-oct-4-en-2-ol (24d), the products of addition of chloral to hex-1-ene ($AlCl_3$ catalysis), is illustrative of the basic procedure.

Ethyl bromide (*ca.* 2 ml) was added to a suspension of magnesium turnings (5.0 g) in dry ether (200 ml) in a 500 ml three-necked flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser together with $CaCl_2$ guard tubes. The mixture was stirred under gentle reflux for *ca.* 5 min, and the crude adduct (24d) + (25d) (46.3 g, 198.2 mmol) was added dropwise during 30 min, the mixture being warmed so that it gently refluxed during the addition and for a further

2 h afterwards. The organic layer was removed from the excess of magnesium and magnesium salts by decantation into a large beaker, and was stirred with 2M-hydrochloric acid (*ca.* 50 ml). After *ca.* 10 min the clear orange organic layer was separated, washed with water (2 × 25 ml) and dried (Na_2SO_4). Filtration and removal of the solvent under reduced pressure afforded a red-brown oil which, on distillation at reduced pressure, afforded the ene adduct as a colourless or pale yellow oil (25.0 g, 77% based on the ene adduct content of the original mixture), b.p. 58—59 °C/0.1 mmHg. Analytical and spectroscopic data are given in the appropriate section below.

Dehydrohalogenation of Trihalogenoketone By-products.—The trihalogenoketone by-products suffered partial or complete dehydrohalogenation [*e.g.* (25d) ⟶ (26)] by passage over t.l.c. grade silica gel G in pressure column chromatography. Since the trihalogenoketone and dihalogenomethyl enone usually possessed near identical R_F values the following dehydrohalogenation procedure was generally more efficient.

The crude adduct mixture (25 mmol) was dissolved in carbon tetrachloride or dichloromethane (20 ml) and pyridine (5 ml) added. After 24 h at room temperature the solution was washed with 2M-hydrochloric acid (3 × 10 ml), saturated aqueous sodium hydrogen carbonate (10 ml), and water (10 ml), and then dried ($MgSO_4$ or Na_2SO_4). Filtration and removal of the solvent under reduced pressure afforded a mixture of the ene adduct and enone, *e.g.* (24d) and (26), which were readily separated by pressure column chromatography and further purified by distillation under reduced pressure.

Conversion of Ene Adducts into their Acetate Esters.—The ene adduct (1 mol equiv.) was dissolved in pyridine (1.2 mol equiv.) and acetic anhydride (1 mol equiv.) added dropwise with stirring. Stirring was continued for 3 h and the mixture then diluted with ether, washed with 2M-hydrochloric acid, saturated aqueous sodium hydrogen carbonate, water, and then dried ($MgSO_4$ or Na_2SO_4). Filtration and removal of the solvent under reduced pressure afforded the crude ene adduct acetate which was purified by distillation under reduced pressure.

Addition Reactions with Chloral

(−)-β-*Pinene*.—Both the thermal [10a] and Lewis acid catalysed additions afforded 1,1,1-*trichloro*-3-{(1S,5S)-6,6-*dimethylbicyclo*[3.1.1]*hept*-2-*en*-2-*yl*}*propan*-2-*ol* (1a) as a mixture of diastereoisomers whose composition depended upon the reaction conditions; [3] b.p. 103—107 °C/0.2 mmHg; t.l.c. R_F 0.49 ($CHCl_3$); $\nu_{max.}$ (film) 3 450, 2 920, 1 090, and 820 cm^{-1}; δ * 5.48 (1 H, m, 3-H), 4.08 [0.*X* H, ddd, separations 2, 5, and 10 Hz, reduced to dd on D_2O shake with loss of 5 Hz splitting, 11-H of (11*R*)-isomer], 4.00 [0.*Y* H, ddd, separations 2, 5, and 10 Hz, reduced to dd on D_2O shake with loss 5 Hz splitting, 11-H of (11*S*)-isomer], 2.87 [1 H, *ca.* dm, separations 2 and 14 Hz, 10-H C*H*(H)], 2.63 [0.*X*H, d, *J* 5 Hz, absent on D_2O shake, OH, (11*R*)-isomer], 2.60 [0.*Y*H, d, *J* 5 Hz, absent on D_2O shake, OH, (11*S*)-isomer], 2.55—2.30 [2 H, m, 10-H CH(*H*) and 7β-H], 2.35—2.20 (2 H, m, 2 × 4-H), 2.16—2.00 (2 H, m, 1-H and 5-H), 1.31 (3 H, s, 3 × 8-H), 1.21 (1 H, d, *J* 8 Hz, 7α-H), and 0.88 (3 H, s, 3 × 9-H); δ_C (11*R*)-isomer 20.9 (q, C-9), 26.2 (q, C-8), 31.2 (t, C-7), 31.6 (t, C-4), 38.0 (s, C-6), 39.7 (t, C-10), 40.5 (d, C-5), 45.3 (d, C-1), 80.4 (d, C-11), 103.7 (s, C-12), 121.0 (d, C-3), and 143.3 (s, C-2); δ_C (11*S*)-isomer 21.2 (q, C-9), 26.2 (q, C-8), 31.3 (t, C-7), 31.6 (t, C-4), 37.7 (s, C-6), 39.3 (t, C-10), 40.5 (d, C-5), 45.8 (d, C-1), 80.7 (d, C-11), 103.7 (s, C-12), 120.5 (d, C-3), and 143.0 (s, C-2) (Found: C, 50.5; H, 6.4. $C_{12}H_{17}Cl_3O$ requires C, 50.8; H, 6.0%); *m*/*z* ($M^{+\cdot}$) 282.0358 ($C_{12}H_{17}{}^{35}Cl_3O^{+\cdot}$ requires 282.0345).

In the thermal reaction traces of an additional compound were detected by t.l.c., i.r., and ^1H n.m.r., and identified as the radical-derived aldehyde (2a) on the basis of spectroscopic comparisons with the bromal product (2b)—see below.

2-*Methylpropene*.—The product 1,1,1-*trichloro*-4-*methylpent*-4-*en*-2-*ol* (5a) had b.p. 93—95 °C/12 mmHg (Found: C, 35.4; H, 4.7. $C_6H_9Cl_3O$ requires C, 35.4; H, 4.4%); *m*/*z* ($M^{+\cdot}$) 201.9737 ($C_6H_9{}^{35}Cl_3O^{+\cdot}$ requires 201.9719); t.l.c. (C_6H_6) R_F 0.34; $n_D{}^{21}$ 1.4954; $\nu_{max.}$ (film) 3 460, 3 080, 2 950, 1 645, 1 090, 895, 820, and 775 cm^{-1}; δ 4.95 (2 H, s, olefinic H), 4.18 (1 H, m, reduced to dd on D_2O shake, separation 2 and 10 Hz, 2-H), 3.20 (1 H, d, *J* 5 Hz, absent on D_2O shake, OH), 2.80 [1 H, d, separation 14 Hz, 3-H C*H*(H)], 2.32 [1 H, dd, separations 10 and 14 Hz, 3-H CH(*H*)], and 1.84 (3 H, s, CH_3).

2-*Methylbut*-1-*ene*.—Reaction afforded a mixture of 1,1,1-trichloro-4-methylenehexan-2-ol (6a) and *E*- and *Z*-1,1,1-trichloro-4-methylhex-4-en-2-ol (7a) which could not be separated; t.l.c. (C_6H_6) single spot R_F 0.35; $\nu_{max.}$ (film) 3 460, 3 050, 2 950, 1 640, 1 100, 895, and 820 cm^{-1}; δ compound (6a) 4.96 (2 H, s, olefin $=CH_2$), 4.13 (1 H, dd, separations 2 and 10 Hz, 2-H), 2.92 (1 H, br s, absent on D_2O shake, OH), 3.0—2.55 [1 H, m, 3-H C*H*(H)], 2.5—2.1 [1 H, m, 3-H CH(*H*)], 2.14 (2 H, *ca.* q, separations 8 Hz, 2 × 5-H), and 1.08 (3 H, t, *J* 7 Hz, CH_3); δ [compounds (7a)] 5.44 (1 H, br m, 5-H), 4.17 (1 H, dd, separations 2 and 10 Hz, 2-H), 2.92 (1 H, br s, absent on D_2O shake, OH), 3.0—2.55 [1 H, m, 3-H C*H*(H)], 2.5—2.1 [1 H, m, 3-H CH(*H*)], and 1.9—1.6 (6 H, m, 2 × CH_3).

2-*Methylenecyclopentane*.—The product 1,1,1-*trichloro*-3-(*cyclopent*-1-*enyl*)*propan*-2-*ol* (8a) was obtained as a colourless oil, b.p. 70—72 °C/0.09 mmHg, which, with time, crystallized, m.p. 41—42 °C; t.l.c. R_F 0.39 (C_6H_6) (Found: C, 41.8; H, 5.15. $C_8H_{11}Cl_3O$ requires C, 41.86; H, 4.83%); $\nu_{max.}$ (KBr) 3 500, 2 950, 2 850, 1 090, 1 035, 810, and 795 cm^{-1}; δ 5.52 (1 H, br s, olefinic H), 4.12 (1 H, dd, separations 2 and 9 Hz, 2-H), 3.28 (1 H, br s, absent on D_2O shake, OH), 2.9—2.6 (6 H, m, 6 × allylic H), and 1.88 (2 H, m, non-allylic ring CH_2).

(+)-*Limonene*.—Reaction afforded a mixture of 1,1,1-*trichloro*-4-(4-*methylcyclohex*-3-*enyl*)*pent*-4-*en*-2-*ol* (9a), E- and Z-1,1,1-*trichloro*-4-(4-*methylcyclohex*-3-*enylidene*)*pentan*-2-*ol* (10a), and 1,1,1-*trichloro*-4-(4-*methylcyclohex*-3-*enyl*)*pent*-3-*en*-2-*ol* (10c) in a ratio 79 : 15 : 6, b.p. 118—123 °C/0.3 mmHg. The three products were separated by pressure column chromatography ($CHCl_3$). *Compound* (9a): t.l.c. R_F 0.47 ($CDCl_3$) (Found: C, 50.9; H, 6.2. $C_{12}H_{17}Cl_3O$ requires C, 50.8; H, 6.0%); *m*/*z* ($M^{+\cdot}$) 282.0330 ($C_{12}H_{17}{}^{35}Cl_3O^{+\cdot}$ requires 282.0344) $n_D{}^{20}$ 1.5234; $\nu_{max.}$ (film) 3 450, 2 950, 1 640, 1 090, 900, 815, and 785 cm^{-1}; δ 5.50 (1 H, m, ring olefinic H), 5.06 (2 H, s, olefinic $=CH_2$), 4.22 (1 H, ddd, separations 2, 5, and 10 Hz, reduced to dd on D_2O shake with loss of 5 Hz splitting, 2-H), 2.98 [1 H, dd, separations 2 and 14 Hz, 3-H C*H*(H)], 2.84 (1 H, d, *J* 5 Hz, absent on D_2O shake, OH), 2.36 [1 H, dd, separations 10 and 14 Hz, 3-H CH(*H*)], 2.30—1.80 (7 H, complex m, 3 × CH_2 and C*H* ring), and 1.67 (3 H, s, CH_3).

E- and *Z*-(10a): t.l.c. R_F 0.51 ($CHCl_3$); i.r. $\nu_{max.}$ (film) 3 450, 2 900, 1 100, 815, and 790 cm^{-1}; δ 5.40 (1 H, m, olefinic H), 4.12 (1 H, dt, separations 4 and 8 Hz, reduced to dd on D_2O

* IUPAC numbering of ring; C-10 is CH_2 of side chain. (0·*X*H + 0.*Y*H) = (1 H).

shake, 2-H), 2.90—2.55 (complex m), 2.38 (m), and 2.05 (m) (total 9 H, 2 × 3-H + OH + 3 × ring CH_2), 1.80 (s) and 1.76 (s) (total 3 H, CH_3 of pentanol chain of *E*- and *Z*-isomers), and 1.67 (3 H, s, ring CH_3).

Compound (10c): t.l.c. R_F 0.44 ($CHCl_3$); $\nu_{max.}$ (film) 3 400, 2 920, 1 660, 1 050, 820, and 780 cm^{-1}; δ 5.45 (2 H, m, olefinic H), 4.87 (1 H, dd, separations 6 and 8 Hz, reduced to d on D_2O shake with loss of 6 Hz splitting, 3-H), 2.70 (1 H, d, absent on D_2O shake, OH), 2.35—1.80 (7 H, complex m, 3 × CH_2 and CH of ring), 1.84 (3 H, s, CH_3 of pentanol chain), and 1.67 (3 H, s, ring CH_3).

In the thermal reaction (135 °C/48 h *in vacuo*) a 16% yield of a mixture of (9a) and *E*- and *Z*-(10a) was obtained (ratio 80.5 : 19.5); compound (10c) was absent.

To a solution of pure (9a) (0.05 g, 0.18 mmol) in CH_2Cl_2 (1 ml) was added $AlCl_3$ (0.71 mg, 3 mol%). Monitoring by t.l.c. after 1.5 h indicated negligible isomerization of the adduct. The concentration of $AlCl_3$ was subsequently increased to 10 mol%, then finally to 50 mol%. Conventional work-up after stirring for a further 1 h afforded the unchanged adduct (9a). Other minor isomers were detectable by t.l.c. but were at a concentration below the sensitivity of 90 MHz ^1H n.m.r.

3-*Methylbuta*-1,2-*diene*.—Reaction in CCl_4 followed by column chromatography afforded only one unstable product from a complex reaction mixture, which was identified as 1,1,1-*trichloro*-3-*methylene*-4-*methylpent*-4-*en*-2-*ol* (11), b.p. 100—110 °C/0.2 mmHg; R_F 0.29 (C_6H_6); $\nu_{max.}$ 3 400, 3 060, 2 900, 1 590, 1 065, and 820 cm^{-1}; δ 5.71, 5.58, 5.17, and 5.12 (all 1 H, m, 2 × olefinic $=CH_2$), 5.07 (1 H, s, 2-H), 3.24 (1 H, br s, absent on D_2O shake, OH), and 2.00 (3 H, s, CH_3).

2-*Methylbut*-2-*ene*.—(*a*) Reaction with 2 mol% $AlCl_3$ in CH_2Cl_2 afforded only 1,1,1-*trichloro*-3,4-*dimethylpent*-4-*en*-2-*ol* (12a), b.p. 60—63 °C/0.5 mmHg, as an 85 : 15 mixture of diastereoisomers, which were separated by pressure column chromatography ($CHCl_3$). The stereochemistry of the major diastereoisomer was determined by single crystal *X*-ray analysis of its 3,5-dinitrobenzoate derivative.[5a] The diastereoisomers were easily resolved by g.l.c. on a 50 m Carbowax 20M glass capillary column, the minor component being eluted first.

Compound (12a): *major diastereoisomer* (*R*,*S* + *S*,*R*); t.l.c. R_F 0.43 ($CHCl_3$) (Found: C, 38.65; H, 5.45. $C_7H_{11}Cl_3O$ requires C, 38.64; H, 5.10%); *m*/*z* ($M^{+\cdot}$) 215.9863 ($C_7H_{11}{}^{35}Cl_3O^{+\cdot}$ requires 215.9875); $\nu_{max.}$ (film) 3 480, 3 080, 2 970, 1 640, 1 130 905 820, and 750 cm^{-1}; δ 4.88 (1 H, m, 5a-H), 4.81 (1 H, m, 5b-H), 4.12 (1 H, dd, separations 3 and 6 Hz, reduced to d on D_2O shake with loss of 6 Hz splitting, 2-H), 2.94 (1 H, qd, separations 3 and 7 Hz, 3-H), 2.90 (1 H, d, *J* 6 Hz, absent on D_2O shake, OH), 1.80 (3 H, s, $=CCH_3$), and 1.22 [3 H, d, *J* 7 Hz, $CH(CH_3)$]; δ_C 148.35 (s, C-4), 111.87 (t, C-5), 104.09 (s, C-1), 83.97 (d, C-2), 42.40 (d, C-3), 20.23 (q, $=CCH_3$), and 13.74 [q, $CH(CH_3)$].

Compound (12a): *minor diastereoisomer* (*R*,*R* + *S*,*S*); t.l.c. R_F 0.46 ($CHCl_3$); i.r. as for major diastereoisomer; δ 4.93 (2 H, br s, 2 × 5-H), 3.97 (1 H, dd, separations 5.5 and 8 Hz, reduced to d on D_2O shake with loss of 8 Hz splitting, 2-H), 2.90 (1 H, qd, separations 5.5 and 7 Hz, 3-H), 2.86 (1 H, d, *J* 8 Hz, absent on D_2O shake, OH), 1.80 (3 H, s, $=CCH_3$), and 1.31 ([3 H, d, *J* 7 Hz, $CH(CH_3)$]; δ_C 145.84 (s, C-4), 114.85 (t, C-5), *ca.* 102 (s, C-1), 84.62 (d, C-2), 43.80 (d, C-3), 20.82 (q, $=CCH_3$), and 19.82 [q, $CH(CH_3)$].

(*b*) Reaction with 10 mol% $AlCl_3$ in CH_2Cl_2 afforded a 55 : 45 mixture of (12a) and 1,1,1,4-*tetrachloro*-3,4-*dimethylpentan*-2-*ol* (13a). Each compound existed as a pair of diastereoisomers (ratio 85 : 15); (12a) and (13a) were inseparable by pressure column chromatography although the diastereoisomeric pairs were resolvable.

Compound (13a): *major diastereoisomer* (*R*,*S* + *S*,*R*); t.l.c. R_F 0.43 ($CHCl_3$); spectroscopic data are listed in section (d) below.

Compound (13a): *minor diastereoisomer* (*R*,*R* + *S*,*S*); t.l.c. R_F 0.46 ($CHCl_3$); δ (by difference from (*R*,*R* + *S*,*S*)-(12a)) 4.56 (1 H, d, *J* 7 Hz, reduced to s on D_2O shake, 2-H), 2.83 (1 H, q, *J* 7 Hz, 3-H), 1.50 [3 H, s, $CH_3C(CH_3)Cl$], 1.43 [3 H, s, $CH_3C(CH_3)Cl$], and 1.20 (3 H, d, *J* 7 Hz, $CHCH_3$); OH signal in region δ 3.10—2.80 obscured by (12a).

(*c*) $FeCl_3$ and Me_2AlCl were also effective catalysts; $SnCl_4$, Et_2AlCl, and $TiCl_4$ were less satisfactory and yields were rather low. The thermal reaction (130 °C for 72 h) gave a trace of (12a) and unknown by-products. Full details relating to the effects of catalyst and reaction conditions are given in the following paper.[5a]

(*d*) *Hydrogenation of* (12a) + (13a). A mixture of (12a) (0.194 g, 0.89 mmol) and (13a) (0.056 g, 0.22 mmol), containing exclusively the major diastereoisomer of each compound, was hydrogenated at room temperature and atmospheric pressure in ethyl acetate solution in the presence of PtO_2 (5 mg). Absorption of 0.89 mmol of hydrogen [*i.e.* 1 equiv. with respect to (12a)] occurred within 2 min, and no further H_2 uptake was observed after this time. Conventional work-up afforded a mixture of 1,1,1-*trichloro*-3,4-*dimethylpentan*-2-*ol* and unchanged (13a) which were separable by pressure column chromatography ($CHCl_3$).

1,1,1-*Trichloro*-3,4-*dimethylpentan*-2-*ol*: (*R*,*S* + *S*,*R*) (0.19 g; 97%), b.p. 56—58 °C/0.2 mmHg (Found: C, 38.4; H, 6.2. $C_7H_{13}Cl_3O$ requires C, 38.30; H, 5.97%); R_F 0.47 ($CHCl_3$); $\nu_{max.}$ (film) 3 580, 3 470, 2 960, 1 140, 815, and 740 cm^{-1}; δ 4.03 (1 H, dd, separations 1.5 and 6.5 Hz, reduced to d on D_2O shake with loss of 6.5 Hz, splitting 2-H), 2.72 (1 H, d, *J* 6.5 Hz, absent on D_2O shake OH), 2.20 (1 H, *ca.* quintet of d, separations 1.5 and 7 Hz, 3-H), 1.77 (1 H, m, 4-H), 1.04 [3 H, d, *J* 7 Hz, $CH(CH_3)CHOH$], and 0.96 [6 H, d, *J* 7 Hz, $CH(CH_3)_2$].

Compound (13a): (*R*,*S* + *S*,*R*); *m*/*z* ($M^{+\cdot}$) not observed, but weak peaks present at 216, 218, and 220 (M − HCl); t.l.c. R_F 0.43 ($CHCl_3$); $\nu_{max.}$ (film) 3 450, 2 970, 1 130, 815, and 740 cm^{-1}; δ 4.56 (1 H, d, *J* 5.5 Hz, reduced to s on D_2O shake, 2-H), 2.87 (1 H, d, *J* 5.5 Hz, absent on D_2O shake, OH), 2.60 (1 H, q, *J* 7 Hz, 3-H), 1.67 [3 H, s, $CH_3C(CH_3)Cl$], 1.60 [3 H, s, $CH_3C(CH_3)Cl$], and 1.22 (3 H, d, *J* 7 Hz, $CHCH_3$).

(*e*) The ene adduct (12a) in CCl_4 solution was treated with $AlCl_3$ (15 mol%). The reaction was monitored by ^1H n.m.r. after 0.5, 2, and 4 h, and the main sample quenched and worked-up in the normal way after a total of 5 h. It was clear that (12a) was converted into (13a) under these conditions as evidenced by development of signals at δ 1.67 and 1.60 [$CH_3C(CH_3)Cl$] and substantial reduction in the 1.80 ($=CCH_3$) and 4.85 ($=CH_2$) signals.

2,3,3-*Trimethylbut*-1-*ene*.—Two products were isolated by pressure column chromatography (C_6H_6): 1,1,1-*trichloro*-4-*methylene*-5,5-*dimethylhexan*-2-*ol* (14) and 2,2,3,3-*tetramethyl*-5-*trichloromethyltetrahydrofuran* (15).

Compound (14): (41%), b.p. 84—86 °C/3 mmHg; t.l.c. R_F 0.41 (C_6H_6); $\nu_{max.}$ (film) 3 450, 2 910, 1 625, 1 405, 1 380, 1 360, 1 195, 1 085, 890, 810, and 790 cm^{-1}; δ 5.17 (1 H, s, $HCH=$), 5.04 (1 H, s, $HCH=$), 4.28 (1 H, dd, separations 2 and 10 Hz, 2-H), 3.00 (1 H, br s, OH), 2.93 (1 H, dd, separations 2 and 16 Hz, 3a-H), 2.37 (1 H, dd, separations 10 and 16 Hz, 3b-H), and 1.15 (9 H, s, 3 × CH_3).

Compound (15): (20%), b.p. 64—66 °C/2 mmHg; t.l.c. R_F 0.67 (C_6H_6); $\nu_{max.}$ (film) 2 930, 1 455, 1 375, 1 160, 1 145, 1 065, and 790 cm^{-1}; δ 4.60 (1 H, dd, separations 7 and 9 Hz,

5-H), 2.09 (2 H, m, 2 × 4-H), 1.30 (3 H, s, *cis*-CH_3 on C-2), 1.23 (3 H, s, *trans*-CH_3 on C-2), 1.11 (3 H, s, *cis*-CH_3 on C-3), and 1.07 (3 H, s, *trans*-CH_3 on C-3).

2-Methyl-3-chloroprop-1-ene.—Reaction in CCl_4 afforded a mixture of four compounds: *1,1,1-trichloro-4-chloromethylpent-4-en-2-ol* (16), E- and Z-*1,1,1,5-tetrachloro-4-methylpent-4-en-2-ol* (17), and *1,1,4,5-tetrachloro-4-methylpentan-2-one* (18); b.p. 85—91 °C/0.2 mmHg; t.l.c. R_F 0.60, 0.39, and 0.28 (C_6H_6); $\nu_{max.}$ (film) 3 500, 2 920, 1 725 (18), 1 635 (16), 1 090, 815 and 775 cm^{-1}; δ 6.0 [br s 5-H for *E*- and *Z*-(17)] 5.89 [s 1-H for (18)] 5.20 and 5.10 [2 × s, 2 × 5-H for (16)], 4.2 [s, CH_2Cl for (16) and (18)], 4.5—3.5 [complex m, 2-H for (16) and (17)], 3.22 [br s, OH for (16) and (17)], 3.0—2.0 [complex m, 3-H for (16) and (17)], 1.91 [s, CH_3 for *E*-(17)], and 1.79 [s, CH_3 for *Z*-(17)]. Integrated intensities were consistent with the assignments indicated, giving an estimated product ratio (16) : *E*-(17) : *Z*-(17) : (18) of *ca.* 9 : 2.3 : 1.4 : 1; δ_C (italicized multiplicities are somewhat uncertain) 16.61 [q, CH_3 (18)], 27.45 [*q*, CH_3 *Z*-(17)], 28.30 [*q*, CH_3 *E*-(17)], 35.26 (t), 39.05 (t), 42.22 (t), 43.92 (t), 48.07 (t), 52.05 (*t*), 54.21 (*t*), 66.37 [s, C-4 (18)], 69.65 (*s*), 69.88 (d), 80.52 (*d*), 81.28 (*d*), 103.16 [s, C-1 for (16) or (17)], 103.39 [s, C-1 for (16) or (17)], 115.55 [d, C-5 for *E*-(17) and *Z*-(17)], 118.24 [t, C-5 for (16)], 133.68 [s, C-4 for *E*-(17)], 140.23 [s, C-4 for *Z*-(17)], and 192.51 [s, C-2 for (18)].

Treatment of the product mixture with pyridine followed by pressure column chromatography afforded *E*-(17): t.l.c. R_F 0.30 (C_6H_6); $\nu_{max.}$ 3 420, 2 910, 1 385, 1 090, 820, and 790 cm^{-1}; δ 5.89 (1 H, br s, 5-H), 4.18 (1 H, dd, separations 2 and 8 Hz, 2-H), 3.1 (1 H, br s, absent on D_2O shake, OH), 2.78 (1 H, br d, *J* 15 Hz, 3a-H), 2.46 (1 H, dd, separations 8 and 15 Hz, 3b-H), and 1.91 (3 H, s, CH_3).

1-Methylcyclohexene.—(*a*) Reaction in CH_2Cl_2 afforded *2,2,2-trichloro-1-(2-methylcyclohex-2-enyl)ethanol* (20), b.p. 82—85 °C/1 mmHg, a 75 : 25 mixture of diastereoisomers which was readily separated by pressure column chromatography ($CHCl_3$) (Found: C, 44.1; H, 5.4; Cl, 42.95. $C_9H_{13}Cl_3O$ requires C, 44.38; H, 5.38; Cl, 43.67%). The minor diastereoisomer eluted first on g.l.c. in a 50 m Carbowax 20M glass capillary column.

Compound (20): major diastereoisomer: t.l.c. R_F 0.47 ($CHCl_3$); $\nu_{max.}$ (film) 3 470, 3 040, 2 930, 1 100, 810, and 755 cm^{1-}; δ 5.74 (1 H, m, olefinic H), 4.44 (1 H, dd, separations 2.5 and 7 Hz, reduced to d on D_2O shake with loss of 7 Hz splitting, 1-H), 2.90 (1 H, m, C*H*CHOH), 2.84 (1 H, d, *J* 7 Hz, absent on D_2O shake, OH), 2.20—1.20 (6 H, complex m, 3 × CH_2 ring), and 1.80 (3 H, s, CH_3).

Compound (20): minor diastereoisomer; t.l.c. R_F 0.50 ($CHCl_3$); $\nu_{max.}$ as for major diasteroisomer; δ 5.76 (1 H, m, olefinic H), 4.02 (1 H, t, *J* 4 Hz, reduced to d on D_2O shake, 1-H), 2.82 (1 H, d, absent on D_2O shake, OH), 2.62 (1 H, m, C*H*CHOH), 2.08 (2 H, m, =CHCH_2), 1.86 (3 H, s, CH_3), and 1.80—1.45 (4 H, m, 2 × CH_2 ring).

Good quality ^1H n.m.r. spectra revealed a minor contaminant in each diasteroisomer of (20). The signals were tentatively assigned to the two diastereoisomers of 2,2,2-trichloro-1-(2-methylenecyclohexyl)ethanol (19) and constituted *ca.* 5% of the adduct mixture; these compounds eluted on g.l.c. in a 50 m Carbowax 20M glass capillary column before the diastereoisomers of (20), the minor isomer of (19) being eluted before the major isomer of (19).

Compound (19): diastereoisomer present in major diastereoisomer of (20); δ 4.76 (2 H, s, $=CH_2$), 4.36 (1 H, m, C*H*OH), and 3.00 (1 H, d, *J* 7 Hz, absent on D_2O shake, OH).

Compound (19): diastereoisomer present in minor diastereoisomer of (20); δ (250 MHz) 4.98 [1 H, m, =C*H*(H)], 4.89 [1 H, m, =CH(*H*)], 4.11 (1 H, dd, separations 6 and 9 Hz, reduced to d on D_2O shake with loss of 9 Hz splitting, C*H*OH), 2.76 (1 H, d, *J* 9 Hz, absent on D_2O shake, OH).

(*b*) Catalysis by Me_2AlCl (100 mol%) in hexane (Method 2) for 3 h afforded mainly (20; 35%); (19) accounted for a very small proportion of the mixture.

(*c*) Catalysis by Et_2AlCl (100 mol%) in hexane–CH_2Cl_2 (Method 1) for 24 h afforded a mixture of isomers (10%). Pressure column chromatography ($CHCl_3$) allowed isolation of (20) and the methylenecyclohexane ene adduct *1,1,1-trichloro-3-cyclohex-1-enylpropan-2-ol* (23) in a 2 : 1 ratio.

Compound (23): isomer of longest retention time on g.l.c. in a 50 m Carbowax 20M glass capillary column; R_F 0.44 ($CHCl_3$); $\nu_{max.}$ (film) 3 460, 2 920, 1 100, 810, and 750 cm^{-1}; δ 5.72 (1 H, m, =CH), 4.20 (1 H, ddd, separations 2.5, 5, and 10 Hz, reduced to dd on D_2O shake with loss of 5 Hz splitting, C*H*OH), 2.80 [1 H, dd, separations 2.5 and 14 Hz, C*H*(H)CHOH], 2.68 (1 H, d, *J* 5 Hz, absent on D_2O shake, OH), 2.30 [1 H, dd, separations 10 and 14 Hz, CH(*H*)CHOH], 2.10 (4 H, complex m, allylic CH_2 ring), and 1.68 (4 H, complex m, 2 × CH_2 ring).

β-*Caryophyllene.*—The original olefin contained isomeric impurities which could not be removed by distillation. After reaction the recovered caryophyllene on g.l.c. analysis exhibited a higher impurity level; this may indicate that the *trans*-isomer is more reactive in the ene sense, or simply that contact with $AlCl_3$ caused some *trans-cis* isomerization in the starting material. Reaction of an excess of olefin with chloral and 2—3 mol% $AlCl_3$ in CCl_4 or CH_2Cl_2 afforded, after work-up, a yellow oil (85%); t.l.c. R_F 0.78, 0.38, 0.26, 0.14, and 0.04 (C_6H_6). Distillation under reduced pressure caused much decomposition, and purification was achieved by pressure column chromatography ($CHCl_3$) which afforded one pure fraction (R_F 0.38). The *adduct* was a colourless oil which partially solidified with time. $\nu_{max.}$ (film) 3 530, 3 030, 2 940, 2 850, 1 640, 1 100, 885, 815, and 785 cm^{-1}; δ 5.26 [1 H, s, =C*H*(H)], 4.95 (2 H, s) and 4.88 (1 H, s) [=CH(*H*) and =CH_2], 6.00 (1 H, dd, separations 2 and 10 Hz, reduced to d on D_2O shake with loss of 10 Hz splitting, C*H*OH), 3.23 (1 H, m, C*H*CHOH), 3.04 (1 H, d, *J* 10 Hz, absent on D_2O shake, OH), 2.6—0.8 (skeletal H), and 1.03 (*ca.* 6 H, s, 2 × CH_3); δ_C 152.4 (s, *C*=CH_2), 148.8 (s, *C*=CH_2), 114.8 (t, C=*C*H_2), 108.8 (t, C=*C*H_2), 103.2 (s, CCl_3), 86.0 (d, CHOH), 55.9 (d, CH), 48.0 (d, CH), 43.4 (d, *C*HCHOH), 41.7 (t, allylic CH_2), 36.3 (t, allylic CH_2), 35.9 (t, CH_2), 33.8 (t, CH_2), 33.3 (s, *C*Me_2), 32.0 (t, CH_2), 30.0 (q, CH_3), and 21.5 (q, CH_3). It was not clear from the ^{13}C n.m.r. spectrum if two diastereoisomers were present. The lack of obvious doubling of some of the resonances indicated that the second diastereoisomer, if present, was only a very minor component.

Some of the chromatography fractions contained very little material; a mixed fraction (R_F 0.26) afforded spectra with several of the features listed above, and it seems likely that a second (minor) ene adduct is formed by addition of chloral to the C=CH_2 unit of β-caryophyllene.

Propene.—Reaction in CCl_4 afforded a 1 : 1 mixture of *1,1,1-trichloropent-4-en-2-ol* (24a) and *1,1,4-trichloropentan-2-one* (25a) which co-distilled. Removal of the ketone by the Grignard procedure afforded pure ene adduct (24a) after distillation, b.p. 80—82 °C/12 mmHg, n_D^{23} 1.4930; t.l.c. R_F 0.23 (C_6H_6) (Found: C, 31.7; H, 3.7. $C_5H_7Cl_3O$ requires C, 31.7; H, 3.7%); *m/z* ($M^{+\cdot}$) 187.9586 ($C_5H_7{}^{35}Cl_3O^{+\cdot}$ requires 187.9562); $\nu_{max.}$ (film) 3 460, 3 080, 2 950, 1 640, 1 080, 1 000, 925, 820, and 785 cm^{-1}; δ 6.20—5.75 (1 H, m, 4-H), 5.40—5.10 (2 H, m, 2 × 5-H), 4.10 (1 H, *ca.* ddd, reduced to dd on

D_2O shake, separations 1.5 and 10 Hz, 2-H), 2.97 (1 H, d, *J* 6 Hz, absent on D_2O shake, OH), 3.05—2.70 (1 H, dd, separations 7 and 15 Hz, 3a-H), 2.60—2.24 (1 H, *ca.* dt approximating to a pentet, separations 7 and 15 Hz, 3b-H).

The ketonic compound was more fully characterized in the analogous reaction of bromal with propene where it was the major product; see below.

Hex-1-ene.—(*a*) Reaction in CH_2Cl_2 ($AlCl_3$ catalysis) afforded a 7 : 3 mixture of 1,1,1-*trichloro-oct-4-en-2-ol* (24d) and 1,1,4-*trichloro-octan-2-one* (25d). Separation was readily achieved by pressure column chromatography but normally resulted in partial dehydrochlorination of (25d) to 1,1-*dichloro-oct-3-en-2-one* (26). Dehydrochlorination was avoided when chromatography was carried out on 50—100 mesh silica gel ($CHCl_3$) using gravity flow. Alternatively, dehydrochlorination could be made to go to completion by use of pyridine as base (see above). Finally, the ene adduct (24d) could be isolated by selectively destroying the trichloroketone (25d) under Grignard-type conditions (see above).

Compound (24d): b.p. 69—70 °C/0.1 mmHg, t.l.c. R_F 0.47 ($CHCl_3$); g.l.c. analysis (25 m Carbowax 20M glass capillary column) indicated that it comprised a 91 : 9 mixture of *E*- : *Z*-isomers (the *Z*-isomer being eluted first) (Found: C, 41.5; H, 5.6. $C_8H_{13}Cl_3O$ requires C, 41.5; H, 5.6%); *m/z* ($M^{+\cdot}$) 230.0021 ($C_8H_{13}{}^{35}ClO^{+\cdot}$ requires 230.0032); $n_D{}^{21}$ 1.4910; $\nu_{max.}$ (film) 3 460, 3 010, 2 950, 1 080, 975, 820, and 790 cm^{-1}; δ 5.62 (1 H, highly perturbed dd, A of AB type, separations 5.5 and 15 Hz, 4-H), 5.48 (1 H, highly perturbed dd, B of AB type, separations 5.5 and 15 Hz, 5-H), 4.02 (1 H, ddd, separations 2.5, 6, and 9.5 Hz, reduced to dd on D_2O shake with loss of 6 Hz splitting, 2-H), 2.92 (1 H, d, *J* 6 Hz, absent on D_2O shake, OH), 2.80—2.50 (1 H, m, 3a-H), 2.40—2.10 (1 H, m, 3b-H), 2.01 (2 H, q, *J* 7 Hz, 2 × 6-H), 1.38 (2 H, *ca.* sextet, separation 7 Hz, 2 × 7-H), and 0.90 (3 H, t, *J* 7 Hz, 3 × 8-H); δ_C 135.2 (d, C-4), 124.6 (d, C-5), 103.8 (s, C-1), 82.9 (d, C-2), 35.5 (t, C-3), 34.7 (t, C-6), 22.5 (t, C-7), and 13.6 (q, C-8).

The *acetate ester* of (24d) was prepared in 78% yield by the procedure outlined above, b.p. 104—106 °C/3.2 mmHg. If the preparation is performed on mixtures of (24d) and (25d) then dehydrochlorination of (25d) to (26) occurs under the reaction conditions. Acetate ester (Found: C, 43.6; H, 5.9. $C_{10}H_{15}Cl_3O_2$ requires C, 43.9; H, 5.5%); t.l.c. R_F 0.63 (C_6H_6).

Compound (25d): b.p. 70—72 °C/0.1 mmHg; t.l.c. R_F 0.76 ($CHCl_3$); $n_D{}^{24}$ 1.4720; *m/z* ($M^{+\cdot}$) absent, ($M^{+\cdot} - C_3H_7$) 186.9466 ($C_5H_6{}^{35}Cl_3O^{+\cdot}$ requires 186.9484); $\nu_{max.}$ (film) 2 900, 1 730, 800, and 750 cm^{-1}; δ 5.87 (1 H, s, 1-H), 4.40 (1 H, m approx. to quintet, 4-H), 3.60—3.00 (2 H, m, AB of ABX, J_{AB} 17 Hz, J_{AX} *ca.* 7.5 Hz, J_{BX} *ca.* 5.5 Hz, 2 × 3-H), 1.78 (2 H, m, 2 × 5-H), 1.42 (4 H, complex m, 2 × 6-H + 2 × 7-H), and 0.95 (3 H, t, *J* 7 Hz, 3 × 8-H).

The *ketone* 2,4-*dinitrophenylhydrazone*, orange-red crystals, m.p. 95—95.5 °C from ethanol (Found: C, 40.6; H, 3.9; N, 13.55. $C_{14}H_{17}Cl_3N_4O_4$ requires C, 40.83; H, 4.13; N, 13.61%); *m/z* ($M^{+\cdot}$) 410.0292 ($C_{14}H_{17}{}^{35}Cl_3N_4O_4{}^{+\cdot}$ requires 410.0315).

Compound (26): b.p. 47—48 °C/0.2 mmHg; t.l.c. R_F 0.74 ($CHCl_3$); $\lambda_{max.}$ (EtOH) 240 nm (log $\varepsilon_{max.}$ 3.96); $\nu_{max.}$ (film) 2 950, 1 700, 1 635, 985, and 790 cm^{-1}; δ 7.20 (1 H, dt, separations 7 and 15 Hz, 4-H), 6.51 (1 H, d, *J* 15 Hz, 3-H), 5.92 (1 H, s, 1-H), 2.29 (2 H, m, 2 × 5-H), 1.38 (4 H, m, 2 × 6-H + 2 × 7-H), and 0.92 (3 H, t, *J* 7 Hz, 3 × 8-H); δ_C 185.0 (s, C-2), 153.4 (d, C-4), 122.0 (d, C-3), 69.7 (d, C-1), 32.6 (t, C-5), 30.0 (t, C-6), 22.3 (t, C-7), and 13.8 (q, C-8).

(*b*) *Reaction catalysed by silica gel.* Brockmann I silica gel was prepared by heating 80—100 mesh material at 160—180 °C *in vacuo* for 4 h. The cooled silica (37 g) was suspended in dry hexane (70 ml) under N_2, and a mixture of anhydrous chloral (3.7 g, 25 mmol) and hex-1-ene (2.1 g, 25 mmol) added dropwise with efficient mechanical stirring. After the mixture had been stirred for 48 h at room temperature the solvent was removed by filtration, and the silica extracted with ether (Soxhlet). The combined organic solutions when evaporated under reduced pressure afforded a 90 : 10 mixture of (24d) : (25d) (1.25 g, 26%).

(*c*) Reaction with chloral in the presence of 100 mol% Et_2AlCl in hexane–CH_2Cl_2 (Method 1) for 2 h afforded a 63 : 37 mixture (40%) of (24d) and 1,1,4-*trichloro-octan-2-ol* (27). Reaction according to Method 2 gave a 64 : 36 ratio of the same products (35%). The two compounds were separated by pressure column chromatography ($CHCl_3$).

Compound (27): *ca.* 15% by Method 1, b.p. 75—78 °C/0.1 mmHg; diastereoisomer ratio 57 : 43 (inseparable by pressure column chromatography) (Found: C, 41.2; H, 6.85. $C_8H_{15}Cl_3O$ requires C, 41.14; H, 6.47%); t.l.c. R_F 0.40 ($CHCl_3$); $\nu_{max.}$ (film) 3 420, 2 960, 1 080, and 790 cm^{-1}; δ (250 MHz) 5.79 (0.43 H, d, *J* 4 Hz, 1-H of diast. 2), 5.72 (0.57 H, d, *J* 4 Hz, 1-H of diast. 1), 4.31—4.03 (2 H, complex m, 2-H + 4-H), 2.78 (1 H, br s, absent on D_2O shake, OH), 2.29—1.93 (2 H, m, 2 × 3-H), 1.82—1.72 (2 H, m, 2 × 5-H), 1.55—1.25 (4 H, complex m, 2 × 6-H + 2 × 7-H), and 0.92 (3 H, t, *J* 7 Hz, 3 × 8-H); D_2O shake and decoupling, irradiation at δ 5.75 (reduces complexity at 4.28 and 4.14, identifies 2-H pair of diastereoisomers), 4.17 (reduces d at 5.79 to s; d at 5.72 to s; reduces m at 2.29—1.93 and 1.82—1.72), and 1.77 (reduces d of t, separations 3.5 and 7 Hz, at 4.21 to dd, one 3.5 Hz splitting lost; reduces complexity at 4.11; identifies 4-H pair of diastereoisomers); δ_C (diastereoisomer 1) 75.98 (d, C-1), 74.16 (d, C-2), 59.93 (d, C-4), 41.17 (t, C-3), 38.76 (t, C-5), 28.52 (t, C-6), 22.23 (t, C-7), and 13.91 (q, C-8); (diastereoisomer 2) 76.39 (d, C-1), 73.75 (d, C-2), 59.93 (d, C-4), 40.93 (t, C-3), 37.73 (t, C-5), 28.40 (t, C-6), 22.23 (t, C-7), and 13.91 (q, C-8).

(*d*) Reaction in the presence of 100 mol% Me_2AlCl in hexane–CH_2Cl_2 (Method 1) for 1.5 g afforded a 71 : 29 mixture (75%) of (24d) and (25d) plus 1,1,4-*trichloro-2-methyloctan-2-ol* (28). Method 2 gave the three products (60%) in a ratio (24d) : (25d) + (28) of 76 : 24. Addition first of chloral and then of hex-1-ene to a solution of Me_2AlCl in hexane gave an increased ratio of 84.5 : 15.5 in 30% yield. The alcohols (24d) and (28) were inseparable by pressure column chromatography ($CHCl_3$). Spectroscopic data for (28) are listed in the following experiment.

Hydrogenation of the mixture of (24d), (25d), *and* (28). A mixture of the above-named compounds [0.50 g, containing 0.35 g, 1.5 mmol of (24d)], dissolved in ethyl acetate (15 ml) was hydrogenated at room temperature and atmospheric pressure in the presence of PtO_2 (10 mg); reduction was complete within 2 min, 1.5 mmol H_2 [*i.e.* 1 mol equiv. relative to (24d)] being absorbed. Conventional work-up afforded a mixture of unchanged (25d), (28), and 1,1,1-*trichloro-octan-2-ol* (29). Pressure column chromatography failed to resolve (29) and (28) adequately, although a small amount of pure (29) was isolated. The two diastereoisomers (*ca.* 50 : 50) of (28) were partially resolved.

Compound (29): b.p. 89—90 °C/0.2 mmHg; t.l.c. R_F 0.50 ($CHCl_3$); $\nu_{max.}$ (film) 3 380, 2 920, 2 850, 1 085, 820, and 780 cm^{-1}; δ 4.00 (1 H, ddd, separations 2, 6, and 10 Hz, reduced to dd on D_2O shake with loss of 6 Hz splitting, 2-H), 2.70 (1 H, d, *J* 6 Hz, absent on D_2O shake, OH), 2.04 (1 H, m, 3a-H), 1.85—1.50 (3 H, complex m, 3b-H + 2 × 4-H), 1.40—1.20 (6 H, complex m, 3 × CH_2), and 0.90 (3 H, t, *J* 7 Hz, 3 × 8-H).

Compound (28): t.l.c. R_F 0.48—0.49 (2 diastereoisomers) ($CHCl_3$); δ [by difference from (29)] 5.90 (0.5 H, s, 1-H of diast. 1), 5.73 (0.5 H, s, 1-H of diast. 2), 4.20 (1 H, m, 4-H), *ca.* 2.70 [1 H, absent on D_2O shake, OH, overlapped by OH of (29)], 2.35—2.00 (2 H, m, 2 × 3-H), 2.00—1.20 (6 H, complex

m, 3 × CH_2), 1.51 (1.5 H, s, CH_3 of diast. 2), 1.45 (1.5 H, s, CH_3 of diast. 1), and 0.90 (3 H, t, *J* 7 Hz, 3 × 8-H).

Oct-1-ene.—Reaction in CCl_4 afforded a 70 : 30 mixture of 1,1,1-*trichlorodec-4-en-2-ol* (24g) and 1,1,4-*trichlorodecan-2-one* (25g). The compounds can be separated as detailed in the chloral/hex-1-ene reaction; data for the major product only is given here.

Compound (24g): g.l.c. assay indicated a 92 : 8 mixture of the *E*- : *Z*-isomers; t.l.c. R_F 0.40—0.42 (C_6H_6), thus enabling separation of the isomers by careful pressure column chromatography (Found: C, 45.9; H, 6.7. $C_{10}H_{17}Cl_3O$ requires C, 46.2; H, 6.6%); *m/z* ($M^{+\cdot}$) 258.0339 ($C_{10}H_{17}{}^{35}Cl_3O^{+\cdot}$ requires 258.0345); $n_D{}^{23}$ 1.4860; $\nu_{max.}$ (film) 3 460, 3 010, 2 900, 1 085, 975, 820, and 790 cm^{-1}; δ (*E*-isomer) 5.52 (2 H, *ca.* qd, separations 6 and 15 Hz, 4-H + 5-H), 4.00 (1 H, m, reduced to dd on D_2O shake, separations 3 and 10 Hz, 2-H), 2.84 (1 H, d, *J* 5.5 Hz, absent on D_2O shake, OH), 2.90—2.64 (1 H, m, 3a-H), 2.48—2.18 (1 H, m, 3b-H), 2.02 (2 H, *ca.* q, *J* 7 Hz, 2 × 6-H), 1.30 (6 H, br m, 3 × CH_2), and 0.88 (3 H, t, *J* 6 Hz, 3 × 10-H); (*Z*-isomer) 5.54 (2 H, *ca.* qd, separations 6 and 10 Hz, 4-H + 5-H), 4.00 (1 H, m, reduced to dd on D_2O shake, separations 3 and 10 Hz, 2-H), 2.84 (1 H, d, *J* 6 Hz, absent on D_2O shake, OH), 2.96—2.66 (1 H, m, 3a-H), 2.56—2.20 (1 H, m, 3b-H), 2.08 (2 H, *ca.* q, *J* Hz, 2 × 6-H), 1.34 (6 H, br m, 3 × CH_2), and 0.88 (3 H, t, *J* 6 Hz, 3 × 10-H).

Octa-1,7-diene.—(*a*) Reaction in CCl_4 using a five-fold excess of olefin and inverse addition afforded, after pyridine treatment and column chromatography, 1,1,1-*trichlorodeca-4,9-dien-2-ol* (24i) and 1,1-*dichlorodeca-3,9-dien-2-one* [(25i) − HCl].

Compound (24i): (31%), b.p. 99—101 °C/0.4 mmHg; t.l.c. R_F 0.38 (C_6H_6) (Found: C, 47.4; H, 5.85. $C_{10}H_{15}Cl_3O$ requires C, 46.83; H, 5.87%); $\nu_{max.}$ (film) 3 460, 3 070, 2 905, 2 840, 1 640, 1 445, 1 090, 980, 825, and 795 cm^{-1}; δ 6.00—5.50 (3 H, m, 4-H + 5-H + 9-H), 5.10—4.90 (2 H, m, 2 × 10-H), 4.04 (1 H, dd, separations 2 and 8 Hz, 2-H), 3.10 (1 H, s, absent on D_2O shake, OH), 2.81 (1 H, m, 3a-H), 2.39 (1 H, m, 3b-H), 2.08 (4 H, m, 2 × 6-H + 2 × 8-H), and 1.50 (2 H, m, 2 × 7-H).

Compound [(25i) − HCl]: (13%), b.p. 90—92 °C/0.5 mmHg; t.l.c. R_F 0.57 (C_6H_6) (Found: C, 54.25; H, 6.3. $C_{10}H_{14}Cl_2O$ requires C, 54.31; H, 6.38%); $\nu_{max.}$ (film) 3 080, 2 930, 2 860, 1 700, 1 635, 1 220, 1 160, 985, 925, 810, and 710 cm^{-1}; δ 7.20 (1 H, dt, separations 7 and 16 Hz, 4-H), 6.56 (1 H, d, *J* 16 Hz, 3-H), 5.98 (1 H, s, 1-H), 5.92 (1 H, m, 9-H), 5.10—4.90 (2 H, m, 2 × 10-H), 2.36 (2 H, m, 2 × 5-H), 2.08 (2 H, m, 2 × 8-H), and 1.50 (4 H, m, 2 × 6-H + 2 × 7-H).

(*b*) Reaction in CCl_4 with a five-fold excess of chloral afforded, after pyridine treatment, esterification, and column chromatography 1,1,1,12,12,12-*hexachlorododeca-4,8-diene-2,11-diol diacetate* [(34) *diacetate*] and 2-*acetoxy*-1,1,1,12,12-*pentachlorododeca-4,9-dien-11-one* [(35) − HCl *acetate*]. *Compound* [(34) *diacetate*] (21%), b.p. 140—148 °C/0.02 mmHg; t.l.c. R_F 0.35 (C_6H_6); $\nu_{max.}$ (film) 3 030, 2 920, 1 780, 1 750, 1 630, 1 375, 1 220, 1 190, 1 040, and 810 cm^{-1}; δ 5.6 (6 H, complex m, olefinic H and CHO), 2.20 (6 H, s, $COCH_3$), and 2.5—1.9 (*ca.* 8 H, complex m, allylic H).

Compound [(35) − HCl *acetate*]: (34%), b.p. 130—140 °C/0.02 mmHg; t.l.c. R_F 0.45 (C_6H_6); $\nu_{max.}$ (film) 3 020, 2 910, 1 745, 1 695, 1 625, 1 370, 1 215, 1 070, and 800 cm^{-1}; δ 7.28 (1 H, m, 9-H), 6.66 (1 H, br d, *J* 16 Hz, 10-H), 6.06 (1 H, s, 12-H), 5.60 (3 H, m, 2-H + 4-H + 5-H), 2.20 (3 H, s, $COCH_3$), and 3.0—1.6 (*ca.* 8 H, complex m, 4 × CH_2).

Allylbenzene.—(*a*) Reaction in CH_2Cl_2 with chloral and 5 mol% $AlCl_3$ for 1 h afforded a 23 : 31 : 46 mixture (50%) of 1,1,1-*trichloro-5-phenylpent-4-en-2-ol* (24j), 1,1,1,4-*tetrachloro-5-phenylpentan-2-ol* (31), and 1,1,4-*trichloro-5-phenylpentan-2-one* (25j). With 10 mol% $AlCl_3$, (31) and (25j) were the exclusive products, formed in a ratio 54 : 46 (65%). Pressure column chromatography ($CHCl_3$) readily separated (25j) from the alcohol products, but (24j) and (31) had identical R_F values and could not be separated. The alcohol (31) was a colourless crystalline solid and pure samples of it were isolated from mixtures of (24j) and (31) by repeated crystallization from pentane. The chloroketone (25j) was best obtained by gravity flow column chromatography on 50—100 mesh silica gel ($CHCl_3$) to avoid contamination by the dehydrochlorination product [(25j) − HCl]. Pure samples of the ene adduct (24j) were obtained by the dehydrochlorination of (31) by 1,5-diazabicyclo[4.3.0]non-5-ene (DBN); mixtures of (24j) and (31) could clearly be used for this purpose.

Compound (25j): t.l.c. R_F 0.80 ($CHCl_3$); *m/z* ($C_{11}H_{11}{}^{35}Cl_3O)^{+\cdot}$ obscured by a marker peak, 265.9813 ($C_{11}H_{11}{}^{35}Cl_2{}^{37}ClO^{+\cdot}$ requires 265.9846); $\nu_{max.}$ (film) 3 020, 2 900, 1 950—1 800 (overtones), 1 740, 1 600, 1 495, 800, 750, and 700 cm^{-1}; δ 7.45—7.10 (5 H, complex m, aryl H), 5.80 (1 H, s, 1-H), 4.57 (1 H, *ca.* quintet, 4-H), 3.45—2.95 (4 H, m, 2 × 3-H + 2 × 5-H).

Compound (31): m.p. 77—78 °C (Found: C, 43.75; H, 4.1. $C_{11}H_{12}Cl_4O$ requires C, 43.74; H, 3.99%); *m/z* ($M^{+\cdot}$) 299.9646 ($C_{11}H_{12}{}^{35}Cl_4O^{+\cdot}$ requires 299.9642); t.l.c. R_F 0.50 ($CHCl_3$); $\nu_{max.}$ (KBr) 3 500, 3 030, 2 930, 1 600, 1 500, 1 100, 810, 790, 755, and 705 cm^{-1}; 250 MHz ^1H n.m.r. δ 7.40—7.20 (5 H, complex m, aryl H), 4.47 (1 H, ddd, J_1 10 Hz, J_2 7 Hz, J_3 2 Hz, reduced to dd on D_2O shake with loss of J_2, 2-H), overlaps with 4.42 (1 H, ddd, J_1 10 Hz, J_2 7 Hz, J_3 2 Hz, 4-H), 3.12 (2 H, d, *J* 7 Hz, 2 × 5-H), 2.96 (1 H, dd, J_1 5 Hz, J_2 2 Hz, absent on D_2O shake, OH), 2.34 (1 H, *ca.* ddt, J_1 14 Hz, J_2 10 Hz, J_3 2 Hz, reduced to ddd on D_2O shake with loss of one 2 Hz splitting, 3a-H), 2.13 (1 H, ddd, J_1 14 Hz, J_2 10 Hz, J_3 2 Hz, 3b-H): decoupling—irradiation at: δ 4.51—4.38 (reduces d at 3.12 to s; dd at 2.96 to d with loss of 5 Hz splitting; ddt at 2.34 to *ca.* dd with loss of 10 Hz, and one 2 Hz splitting; ddd at 2.13 to d with loss of 2 and 10 Hz splittings), 3.12 (reduces ddd at 4.12 to dd with loss of 7 Hz splitting); identifies 4-H specifically, and hence Cl substitution at C-4); δ_C 137.14 (s, aryl C-1), 129.38 (d, aryl C-2 + C-6), 128.56 (d, aryl C-3 + C-5), 127.06 (d, aryl C-4), 103.39 (s, C-1), 80.27 (d, C-2), 59.81 (d, C-4), 45.28 (t, C-5), and 39.67 (t, C-3).

Compound (24j). To a solution of (31) (0.155 g, 0.51 mmol) in dry THF (0.5 ml) was added dropwise, with stirring, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (0.3 g, 2.4 mmol). The solution was boiled under reflux for 2 h during which time the mixture darkened from yellow to brown and DBN·HCl precipitated. The mixture was diluted with ether (15 ml), washed with 1M-sulphuric acid (2 × 5 ml) and water (5 ml), and then dried ($MgSO_4$). Filtration followed by solvent removal under reduced pressure afforded the ene adduct (24j) (0.10 g, 74%) as a viscous oil which was chromatographed on a short silica column (CH_2Cl_2), and distilled, b.p. 102—105 °C/0.2 mmHg; t.l.c. R_F 0.50 ($CHCl_3$); $\nu_{max.}$ (film) 3 450, 3 025, 2 920, 1 950—1 750 (overtones), 1 600, 1 500, 1 100, 975, 790, 755, and 700 cm^{-1}; δ 7,45—7.20 (5 H, complex m, aryl H), 6.58 (1 H, d, *J* 16 Hz, 5-H), 6.30 (1 H, dt, J_1 16 Hz, J_2 6.5 Hz, 4-H), 4.16 (1 H, ddd, separations 2.5, 5.5, and 9 Hz, reduced to dd on D_2O shake with loss of 5.5 Hz splitting, 2-H), 2.97 (1 H, ddd, separations 2.5, 6.5, and 14 Hz, 3a-H), 2.92 (1 H, d, *J* 5.5 Hz, absent on D_2O shake, OH), and 2.63 (1 H, ddd, separations 6.5, 9, and 14 Hz, 3b-H).

1,1-*Dichloro-5-phenylpent-3-en-2-one* [(25j) − HCl]. The trichloroketone (25j) was dehydrochlorinated by treatment with pyridine as outlined in the general procedure above, and

the crude product (66%) was purified by pressure column chromatography ($CHCl_3$–hexane 3:1 v/v) and distillation, b.p. 90—92 °C/0.2 mmHg; *m/z* ($M^{+\cdot}$) 228.0113 ($C_{11}H_{10}{}^{35}Cl_2O^{+\cdot}$ requires 228.0108); t.l.c. R_F 0.76 ($CHCl_3$); $\nu_{max.}$ (film) 3 020, 2 950, 2 880, 1 950—1 800 (overtones), 1 700, 1 625, 990, 805, 760, and 700 cm^{-1}; δ 7.50—7.15 (6 H, complex m, aryl H + 4-H), 6.03 (1 H, dd, J_1 16 Hz, J_2 1.5 Hz, 3-H), 5.90 (1 H, s, 1-H), and 3.58 (2 H, dd, J_1 7 Hz, J_2 1.5 Hz, 2 × 5-H).

(*b*) Reaction using 100 mol% Me_2AlCl in hexane–CH_2Cl_2 (Method 1) for 1.5 h afforded a mixture of (24j), (25j), and 1,1,4-*trichloro*-2-*methyl*-5-*phenylpentan*-2-*ol* (33) in a ratio 59 : 41 for (24j) : (25j) + (33) in 55% yield. Pressure column chromatography ($CHCl_3$) failed to separate (24j) from (33), but the two diastereoisomers of (33), present in 50 : 50 ratio, were partially resolved.

Compound (33): t.l.c. R_F 0.49—0.50 (2 diastereoisomers) ($CHCl_3$); δ [by difference from (24j)] 7.45—7.25 (5 H, complex m, aryl H), 5.89 (0.5 H, s, 1-H diast. 1), 5.68 (0.5 H, s, 1-H diast. 2), 4.45 (1 H, m, 4-H), 3.10 (2 H, d, *J* 7 Hz, 2 × 5-H), 2.60 (1 H, s, absent on D_2O shake, OH), 2.40—2.10 (2 H, m, 2 × 3-H), 1.50 (1.5 H, s, CH_3 diast. 2), and 1.36 (1.5 H, s, CH_3 diast. 1).

Allyl Bromide.—Reaction in CCl_4 in the presence of 10 mol% $AlCl_3$ for 6 h afforded a ketone identified as 5-*bromo*-1,1,4-*trichloropentan*-2-*one* (25k), b.p. 76—79 °C/0.15 mmHg; *m/z* ($M^{+\cdot}$) 266 (very weak), ($M^{+\cdot}$ − ^{35}Cl) 230.8952 ($C_5H_6{}^{79}Br^{35}Cl_2O^{+\cdot}$ requires 230.8980), 183 (M − $CHCl_2$), 155 (M − $COCHCl_2$), 147 (M − $CHCl_2$ − HCl), and 119 (M − $COCHCl_2$ − HCl); t.l.c. R_F 0.55 (C_6H_6); $\nu_{max.}$ (film) 2 950, 1 730, 800, and 750 cm^{-1}; δ 5.96 (1 H, s, 1-H), 4.7—4.4 (*ca.* 1 H, complex m, 4-H), 3.9—3.2 (4 H, complex m, 2 × 3-H + 2 × 5-H).

Ethyl Nona-3,8-*dienoate*.—Reaction was conducted in the presence of 50 mol% $AlCl_3$ in dry benzene under N_2 at room temperature for 7 days in a Carius tube equipped with a high vacuum Teflon screw valve. Distillation of the crude product, b.p. 121—125 °C/0.05 mmHg, afforded a colourless oil (58%) which was purified by pressure column chromatography ($CHCl_3$) and Kugelröhr distillation to give *ethyl* 11,11,11-*trichloro*-10-*hydroxyundeca*-3,7-*dienoate* (24l) (43%) and *ethyl* 11,11-*dichloro*-10-*oxoundeca*-3,8-*dienoate* (25l) (11%).

Compound (24l): b.p. 125 °C/0.05 mmHg; t.l.c. R_F 0.25 ($CHCl_3$) (Found: C, 47.4; H, 5.9. $C_{13}H_{19}Cl_3O_3$ requires C, 47.3; H, 5.8%); $\nu_{max.}$ (film) 3 450, 3 050, 2 920, 1 720, 1 640, 1 180, 1 030, 970, 910, 800, and 740 cm^{-1}; δ 5.48 (4 H, complex m, 3-H + 4-H + 7-H + 8-H), 4.08 (2 H, q, *J* 7 Hz, OCH_2), 3.84 (1 H, m, reduced on D_2O shake to dd, separations 3 and 10 Hz, 10-H), 3.74 (1 H, br s, absent on D_2O shake, OH), 2.96 (2 H, m, 2 × 2-H), 2.78—2.64 (1 H, complex m, 9a-H), 2.28 (1 H, m, 9b-H), 2.12 (4 H, m, 2 × 5-H + 2 × 6-H), and 1.24 (3 H, t, *J* 7 Hz, CH_3); δ_C 172.1 (s, C-1), 133.9 (d, =C), 133.7 (d, =C), 125.3 (d, =C), 122.3 (d, =C), 103.7 (s, C-11), 82.5 (d, C-10), 60.6 (t, OCH_2), 38.1 (t, C-2), 35.2 (t, C-9), 31.9 (2 × t, C-5 + C-6), and 14.2 (q, CH_3).

Compound (25l): b.p. 83 °C/0.05 mmHg; t.l.c. R_F 0.42 ($CHCl_3$); $\nu_{max.}$ (film) 3 020, 2 900, 1 740, 1 700, 1 630, 1 180, 975, and 800 cm^{-1}; δ 7.20 (1 H, dt, J_1 16 Hz, J_2 7 Hz, 8-H), 6.58 (1 H, d, *J* 16 Hz, 9-H), 5.86 (1 H, s, 11-H), 5.54 (2 H, m, 3-H + 4-H), 4.12 (2 H, q, *J* 8 Hz, OCH_2), 3.00 (2 H, m, 2 × 2-H), 2.34 (2 H, m, 2 × 7-H), 2.12 (2 H, m, 2 × 5-H), 1.64 (2 H, m, 2 × 6-H), and 1.28 (3 H, t, *J* 8 Hz, CH_3); δ_C 173.1 (s, C-10), 172.1 (s, C-1), 153.2 (d, C-8), 133.3 (d, C-9), 123.0 (d, C-3 or C-4), 122.0 (d, C-4 or C-3), 69.6 (d, C-11), 60.6 (t, OCH_2), 38.1 (t, C-2), 32.2 (t, C-7), 31.8 (t, C-5), 27.3 (t, C-6), and 14.2 (q, CH_3).

Hex-1-*yne*.—Reaction in CH_2Cl_2 in the presence of 6 mol% $AlCl_3$ for 7—20 h afforded a brownish oil after work-up (71%). Distillation under reduced pressure b.p. 80—100 °C/0.5 mmHg, gave a colourless oil (48%) which partially crystallized to a white waxy solid. Recrystallization from light petroleum or methanol gave a pure sample of (38). However, as the oil comprised a mixture of compounds it was more convenient to purify the total crude reaction product by pressure column chromatography ($CHCl_3$). Three fractions afforded pure materials directly: 1,1,4-*trichloro*-*oct*-3-*en*-2-*one* (36), 1,1,1-*trichloro*-*octa*-3,4-*dien*-2-*ol* (37) as a single diastereoisomer, and 1,1,1,4-*tetrachloro*-*oct*-3-*en*-2-*ol* (38). G.l.c. analysis of the crude product using a 25 m Carbowax 20M glass capillary column indicated the presence of five compounds, and peak areas (in order of elution) were 5 : 23 : 22.5 : 6 : 43.5. Compounds (36), (37), and (38) were responsible, respectively, for the first, second, and last g.l.c. peaks. A mixed fraction from chromatography, comprising entirely the second and third g.l.c. peaks, consisted of a mixture of the two diastereoisomers of (37). Re-chromatography of a mixed fraction enabled the separation of a small sample of the second diastereoisomer of (37). The g.l.c. f.i.d. detector sensitivity towards enone (36) appeared to be low, possibly due to electron-capture, and hence peak area is not a good measure of its relative importance in the product mixture.

Compound (36): (10%), t.l.c. R_F 0.4 ($CHCl_3$) (Found: C, 41.7; H, 4.85. $C_8H_{11}Cl_3O$ requires C, 41.86; H, 4.83%); $\nu_{max.}$ (film) 3 020, 2 960, 2 930, 2 860, 1 710, 1 605, 1 165, and 785 cm^{-1}; δ 6.76 (1 H, s, 3-H), 5.84 (1 H, s, 1-H), 2.60 (2 H, t, *J* 7 Hz, 2 × 5-H), 1.82—1.20 (4 H, complex m, 2 × 6-H + 2 × 7-H), and 0.96 (3 H, t, 3 × 8-H); δ_C 182.98 (s, C-2), 156.87 (s, C-4), 115.76 (d, C-3), 70.25 (d, C-1), 41.90 (t, C-5), 29.49 (t, C-6), 21.73 (t, C-7), and 13.67 (q, C-8).

Compound (37). Diastereoisomer 1 (7%), t.l.c. R_F 0.32 ($CHCl_3$) (Found: C, 41.4; H, 4.85. $C_8H_{11}Cl_3O$ requires C, 41.86; H, 4.83%); $\nu_{max.}$ (film) 3 430, 3 010, 2 960, 2 920, 2 860, 1 960, 1 745, 1 635, 1 460, 1 375, 820, and 790 cm^{-1}; δ (CCl_4) 5.20 (2 H, *ca.* dd, separations 4 and 7 Hz, 3-H + 5-H), 4.25 (1 H, t, separation 4 Hz, 2-H), 3.34 (1 H, br s, absent on D_2O shake, OH), 1.96 (2 H, *ca.* pentet, separations 6 Hz, 2 × 6-H), 1.40 (2 H, *ca.* sextet, separations 7 Hz, 2 × 7-H), and 0.92 (3 H, t, *J* 7 Hz, 3 × 8-H); δ_C 204.59 (s, C-4), 103.09 (s, C-1), 96.98 (d, C-3), 89.48 (d, C-5), 80.30 (d, C-2), 30.37 (t, C-6), 22.29 (t, C-7), and 13.61 (q, C-8).

Diastereoisomer 2: t.l.c. R_F 0.30 ($CHCl_3$); δ 5.53 (2 H, m, approx. dd, separations 5 and 14 Hz, 3-H + 5-H), 4.58 (1 H, unsymm. t, separations 3.5 and 4 Hz, 2-H), 3.55 (1 H, br s, absent on D_2O shake, OH), 2.07 (2 H, *ca.* pentet, separations 6 Hz, 2 × 6-H), 1.51 (2 H, *ca.* sextet, separations 7 Hz, 2 × 7-H), and 0.94 (3 H, t, *J* 7 Hz, 3 × 8-H).

Compound (38): (30%), t.l.c. R_F 0.2 ($CHCl_3$), m.p. 70—71 °C (Found: C, 36.5; H, 4.75. $C_8H_{12}Cl_4O$ requires C, 36.12; H, 4.55%); $\nu_{max.}$ (KBr) 3 280, 2 940, 2 860, 1 660, 1 050, 825, and 785 cm^{-1}; δ 5.65 (1 H, d, *J* 8 Hz, 3-H), 5.00 (1 H, dd, separations 5 and 8 Hz, reduced to d on D_2O shake with loss of 5 Hz splitting, 2-H), 2.79 (1 H, d, *J* 5 Hz, absent on D_2O shake, OH), 2.36 (2 H, t, *J* 7 Hz, 2 × 5-H), 1.65—1.07 (4 H, complex m, 2 × 6-H + 2 × 7-H), and 0.83 (3 H, t, *J* 7 Hz, 3 × 8-H); δ_C 143.58 (s, C-4), 120.32 (d, C-3), 102.33 (s, C-1), 79.98 (d, C-2), 39.58 (t, C-5), 29.20 (t, C-6), 21.58 (t, C-7), and 13.70 (q, C-8).

cis- *and* trans-*But*-2-*ene*.—The reactions were conducted in CH_2Cl_2 in the presence of 6 mol% $AlCl_3$ according to general procedure (2). After 1 h t.l.c. analysis indicated the formation of addition products, and reaction of the *cis*-alkene was decidedly faster. Work-up (after 3–4 h or after stirring overnight) afforded brownish oils (80—90% from the *cis*-olefin,

60—68% from the *trans*-olefin). T.l.c. analysis of the crude product from the *cis*-but-2-ene reaction indicated the presence of two products, identified from spectroscopic data as the ene adduct 1,1,1-*trichloro*-3-*methylpent*-4-*en*-2-*ol* (39a) and the ketone 1,1,4-*trichloro*-3-*methylpentan*-2-*one* (40a), formed in a ratio *ca.* 3 : 2. Similar analysis of the products from the *trans*-but-2-ene reaction indicated the presence of (39a), (40a), and the hydrochlorinated derivative 1,1,1,4-*tetrachloro*-3-*methylpentan*-2-*ol* (41) formed in a ratio *ca.* 2 : 73 : 25. The ketone (40a) was removed by chromatography on 100—200 mesh silica gel ($CHCl_3$) with gravity flow; pressure column chromatography ($CHCl_3$) succeeded in separating the alcohols (39a) and (41). The ene adduct (39a) from the *cis*-but-2-ene reaction consisted of a *ca.* 3 : 1 mixture of diastereoisomers; since (39a) was formed in only trace quantities in the *trans*-but-2-ene reaction it was not possible to detect the minor diastereoisomer. Although (40a) and (41) can exist in diastereoisomeric modifications, these were not detected.

Compound (39a): t.l.c. R_F 0.55 ($CHCl_3$); $\nu_{max.}$ (film) 3 550, 3 080, 2 990, 1 645, 1 000, 910, 815, and 765 cm^{-1}; δ (CCl_4) (major diastereoisomer) 6.36—5.94 (1 H, m, 4-H) 5.36—5.08 (2 H m 2 × 5-H), 4.05 (1 H, d, *J* 2 Hz, 2-H), 3.15 (1 H, br pentet, *J* ca. 7 Hz, 3-H), 3.07 (1 H, br s, absent on D_2O shake, OH), and 1.33 (3 H, d, *J* 7 Hz, CH_3); δ_C 141.35 (d, C-4), 114.74 (t, C-5), 103.71 (s, C-1), 84.80 (d, C-2), 40.02 (d, C-3), and 14.61 (q, CH_3).

Minor diastereoisomer: (1 H, d, *J* 2 Hz, 2-H) *ca.* 0.16 p.p.m. upfield from the corresponding resonance for the major diastereoisomer.

Compound (40a): t.l.c. R_F 0.81 ($CHCl_3$); $\nu_{max.}$ (film) 2 970, 2 920, 1 745, 1 455, 1 385, 810, and 755 cm^{-1}; δ 6.11 (1 H s, 1-H), 4.17 (1 H, dq, separations 7 and 9 Hz, 4-H), 3.38 (1 H, dq, separations 7 and 9 Hz, 3-H), 1.60 (3 H, d, *J* 7 Hz, 3 × 5-H), and 1.30 (3 H, d, *J* 7 Hz, CH_3 at C-3).

Compound (41): t.l.c. R_F 0.58 ($CHCl_3$); $\nu_{max.}$ (film) 3 550, 2 990, 1 040, 815, and 760 cm^{-1}; δ 4.50 (1 H, dd, separations 1.5 and 5.5 Hz, reduced to d on D_2O shake with loss of 5.5 Hz splitting, 2-H), 4.19 (1 H, pentet, separations 7 Hz, 4-H), 3.00 (1 H, d, *J* 5.5 Hz, absent on D_2O shake, OH), 2.66 (1 H, pentet, separations 7 Hz, 3-H), 1.65 (3 H, d, *J* 7 Hz, 3 × 5-H), and 1.29 (3 H, d, *J* 7 Hz, CH_3 at C-3); δ_C 103.71 (s, C-1), 81.60 (d, C-2), 61.96 (d, C-4), 42.31 (d, C-3), 22.52 (q, C-5), and 10.94 (q, CH_3 at C-3); *m/z* $M^{+\cdot}$ absent, 220 ($M - H_2O$), and 202 (M − HCl).

Cyclopentene.—Reaction in CCl_4 or CH_2Cl_2 afforded after work-up a pale yellow oil; both t.l.c. and ^1H n.m.r. analysis indicated the predominance of the ene adduct 2,2,2-*trichloro*-1-(*cyclopent*-2-*enyl*)*ethanol* (39b) over the ketonic product 2,2-*dichloro*-1-(2-*chlorocyclopentyl*)*ethanone* (40b), ratio *ca.* 95 : 5. The ketone (40b) was readily removed by column chromatography or by selective decomposition using the Grignard procedure above. The ene adduct consisted of a *ca.* 91 : 9 mixture of diastereoisomers.

Compound (39b): t.l.c. R_F 0.40 ($CHCl_3$), b.p. 65—68 °C/0.1 mmHg; $\nu_{max.}$ (film) 3 530, 3 070, 2 960, 2 860, 1 630, 1 100, 1 025, 820, and 725 cm^{-1}; δ (major diastereoisomer) (CCl_4) 6.12—5.88 (2 H, complex m, olefinic H), 4.00 (1 H, d, *J* 4 Hz, C*H*OH), 3.64—3.40 (1 H, br m, C*H*CHOH), 3.20 (1 H, br s, absent on D_2O shake, OH), 2.56—1.68 (4 H, complex m, 2 × CH_2); δ (minor diastereoisomer) (CCl_4) 4.12 (1 H, d, *J* 3 Hz, C*H*OH).

That the minor component of (39b) was a diastereoisomer was proven by hydrogenating the mixture to give dihydro-(39b); $\nu_{max.}$ (film) 3 500, 2 950, 2 850, 1 100, 1 040, and 820 cm^{-1}; δ 3.98 (1 H, d, *J* 5 Hz, C*H*OH), 2.86 (1 H, br s, absent on D_2O shake, OH), 2.46 (1 H, br m, C*H*CHOH), and 2.00—1.36 (8 H, br m, 4 × CH_2). The removal of the ring C=C also removed the chirality of the ring C*H* atom, and led to the collapse of the δ 4.00 and 4.12 C*H*OH signals in (39b) to a single signal at δ 3.98 for dihydro-(39b).

The minor product (40b) was characterized by differences in the spectroscopic parameters for the crude product and pure (39b) only; $\nu_{max.}$ (film) 1 740 cm^{-1}; δ (CCl_4) 6.04 (s, $CHCl_2$) and 4.52 (br m, CHCl); also by t.l.c. R_F 0.59 ($CHCl_3$) characteristic negative stain with I_2 vapour as shown by all of the dichloromethyl ketones.

In some reactions, after more prolonged contact of (39b) with the $AlCl_3$, the products were contaminated with a third compound, probably the cyclic ether 3-trichloromethyl-2-oxabicyclo[2.2.1]heptane.[9]

Cyclohexene.—In the conventional reactions in CCl_4 or CH_2Cl_2 solutions in the presence of 6 mol% $AlCl_3$, prolonged contact of the ene product with the catalyst promoted a cyclisation reaction,[9] and hence optimum conversions required t.l.c. monitoring of the reaction *versus* time. In the absence of solvent the ene addition was rapid in the presence of 10 mol% $AlCl_3$; work-up after 2 h afforded an 88 : 12 mixture (62%) of the ene adduct 2,2,2-*trichloro*-1-(*cyclohex*-2-*enyl*)*ethanol* (39c) and ketonic by-product 2,2-*dichloro*-1-(2-*chlorocyclohexyl*)*ethanone* (40c). The two products were readily separated by pressure column chromatography ($CHCl_3$), and the two diastereoisomers of (39c) were also resolved; g.l.c. assay on a 25 m OV-17 glass capillary column revealed that the diastereoisomer ratio (*R*,*R* + *S*,*S*): (*R*,*S* + *S*,*R*) was 87 : 13, the major isomer possessing the shorter retention time. Stereochemical assignments are based on single crystal *X*-ray studies [3c,5a] of the toluene-*p*-sulphonate ester of the major diastereoisomer, m.p. 120—121 °C.

Compound (39c): b.p. 78—80 °C/1.5 mmHg (Found: C, 41.6; H, 5.1. $C_8H_{11}Cl_3O$ requires C, 41.8; H, 4.8%); *m/z* ($M^{+\cdot}$) 227.9890 ($C_8H_{11}{}^{35}Cl_3O^{+\cdot}$ requires 227.9875); $n_D^{26.5}$ 1.5250; $\nu_{max.}$ (film) 3 500, 3 030, 2 940, 1 100, and 820 cm^{-1}.

Major diastereoisomer: δ 6.00 (2 H, m, olefinic H), 3.96 (1 H, dd, separations 2 and 8 Hz, reduced to d on D_2O shake with loss of 8 Hz splitting, C*H*OH), 3.02 (1 H, m, C*H*CHOH), 2.80 (1 H, d, *J* 8 Hz, absent on D_2O shake, OH), 2.05 (2 H, m, allylic CH_2), and 1.90—1.50 (4 H, m, 2 × CH_2 ring); t.l.c. R_F 0.43 ($CHCl_3$).

Minor diastereoisomer: δ 5.90 (1 H, dm, J_1 10.5 Hz, CH_2CH=C*H*CH), 5.71 (1 H, dm, J_1 10.5 Hz, CH_2CH=CHCH), 4.13 (1 H, dd, separations 4 and 6 Hz, reduced to d on D_2O shake with loss of 6 Hz splitting, C*H*OH), 2.96 (1 H, m, C*H*CHOH), 2.84 (1 H, d, *J* 6 Hz, absent on D_2O shake, OH), and 2.30—1.50 (6 H, complex m, 3 × CH_2 ring); t.l.c. R_F 0.35 ($CHCl_3$).

Compound (40c): b.p. 82—84 °C/1.5 mmHg; shorter retention time than (39c) by g.l.c. on the above capillary column; t.l.c. R_F 0.59 ($CHCl_3$); $\nu_{max.}$ (film) 2 940, 2 860, 1 740, 805, and 755 cm^{-1}; δ 6.20 (1 H, s, $CHCl_2$), 4.72 (1 H, *ca.* q, *J* 3.5 Hz, CHCl), 3.40 (1 H, m, CHCO), and 2.40—1.30 (8 H, complex m, 4 × CH_2 ring).

Cycloheptene.—Reaction as for cyclopentene or cyclooctene afforded a brownish oil which was shown by t.l.c. and ^1H n.m.r. analysis to consist of a *ca.* 40 : 60 mixture of the ene adduct (39e) and ketone (40e) with variable quantities of a third component as a contaminant; this compound is most probably a cyclic ether.[9] An additional minor contaminant also appeared to be present with a similar R_F value to the ene adduct; in view of other results described above it seems likely that this compound is the hydrochlorinated ene adduct. Only the ene adduct, 2,2,2-*trichloro*-1-(*cyclohept*-2-*enyl*)-*ethanol* (39e), and the ketone, 2,2-*dichloro*-1-(2-*chlorocycloheptyl*)*ethanone* (40e), were isolated in a state of purity, the

separation being effected by chromatography over 100—200 mesh silica gel ($CHCl_3$) using gravity flow. The fractions containing (39e) were further purified by pressure column chromatography ($CHCl_3$).

Compound (39e): $\nu_{max.}$ (film) 3 450, 3 010, 2 930, 2 860, 1 640, 1 440, 1 100, 1 080, 1 045, 820, and 785 cm^{-1}; δ 6.05 (2 H, m, olefinic H), 4.24 (1 H, d, *J* 2 Hz, C*H*OH), 3.10 (1 H, br m, C*H*CHOH), 3.05 (1 H, br s, absent on D_2O shake, OH), 2.25 (2 H, br m, allylic CH_2), and 2.1—1.6 (6 H, br complex m, 3 × CH_2 ring); t.l.c. R_F 0.39 ($CHCl_3$).

Compound (40e): $\nu_{max.}$ (film) 2 930, 2 850, 1 740, 1 460, 1 445, 1 085, 795, and 685 cm^{-1}; δ 6.08 (1 H, s, $CHCl_2$), 4.70 (1 H, *ca.* dt, separations 3 and 8 Hz, CHCl), 3.48 (1 H, m, CHCO), and 2.56—1.35 (10 H, complex m, 5 × CH_2 ring); t.l.c. R_F 0.60 ($CHCl_3$).

Cyclo-octene.—Reaction in CCl_4 with 6 mol% $AlCl_3$ for 4 h afforded an orange viscous oil (75%) comprising almost entirely the ene adduct 2,2,2-*trichloro*-1-(*cyclo-oct*-2-*enyl*)-*ethanol* (39g). A small quantity (<5%) of the ketone 2,2-*dichloro*-1-(2-*chlorocyclo-octyl*)*ethanone* (40g) was detected, but was readily destroyed by the Grignard procedure described above.

Compound (39g): b.p. 105—106 °C/0.01 mmHg; t.l.c. R_F 0.48 (C_6H_6) (Found: C, 46.9; H, 5.7. $C_{10}H_{15}Cl_3O$ requires C, 46.63; H, 5.87%); $\nu_{max.}$ (film) 3 500, 3 030, 2 930, 2 860, 1 650, 1 460, 1 115, 810, 745, and 710 cm^{-1}; δ (major diastereoisomer) 5.72 (2 H, complex m, olefinic H), 4.04 (1 H, d, *J* 2 Hz, C*H*OH), 3.40 (1 H, br m, C*H*CHOH), 3.09 (1 H, br s, absent on D_2O shake, OH), 2.12 (2 H, br m, allylic CH_2), 1.9—1.1 (*ca.* 8 H, br m, 4 × CH_2 ring); δ (minor diastereoisomer) 4.22 (d, *J* 3.5 Hz), isomer ratio >94 : 6.

On hydrogenation of (39g) only one signal was observed for the C*H*OH proton, confirming that the δ 4.04 and 4.22 signals were due to the two diastereoisomers of the ene adduct. *X*-Ray crystallographic analysis of the toluene-*p*-sulphonate ester of the major diastereoisomer, m.p. 85.5—86.5 °C, showed that it possessed the same relative configurtion at the two chiral centres, *i.e.* (*R*,*R* + *S*,*S*).[3c,5a]

1-*Chlorocyclohexene*.—Reaction in CH_2Cl_2 in the presence of 5 mol% $AlCl_3$ for 24 h afforded a 67 : 33 mixture (27%) of the ene adduct 2,2,2-*trichloro*-1-(2-*chlorocyclohex*-2-*enyl*)-*ethanol* (42) and 2,2,2-*trichloro*-1-(2,2-*dichlorocyclohexyl*)-*ethanol* (43); (42) was present as a 57 : 43 mixture of diastereoisomers, and the minor diastereoisomer was isolated in a pure state by pressure column chromatography ($CHCl_3$), but the major diastereoisomer of (42) and the hydrochlorinated adduct (43) were not satisfactorily resolved.

Compound (42): minor diastereoisomer (8%), b.p. 107—109 °C/0.2 mmHg; t.l.c. R_F 0.49 ($CHCl_3$) (Found: C, 36.0; H, 3.9. $C_8H_{10}Cl_4O$ requires C, 36.40; H, 3.82%); $\nu_{max.}$ (film) 3 550, 3 040, 2 930, 1 645, 1 110, 815, 785, and 755 cm^{-1}; δ 6.14 (1 H, m, olefinic H), 4.10 (1 H, dd, separations 4.5 and 10 Hz, reduced to d on D_2O shake with loss of 10 Hz splitting, C*H*OH), 3.26 (1 H, d, *J* 10 Hz, absent on D_2O shake, OH), 2.97 (1 H, m, C*H*CHOH), and 2.30—1.50 (6 H, complex m, 3 × CH_2 ring).

Major diastereoisomer: (9.5%); t.l.c. R_F 0.43 ($CHCl_3$); δ 6.14 (1 H, m, olefinic H), 4.80 (1 H, d, *J* 6 Hz, reduced to s on D_2O shake, C*H*OH), 3.24 (1 H, d, *J* 6 Hz, absent on D_2O shake, OH), 3.14 (1 H, m, C*H*CHOH), and 2.40—1.50 (4 H, complex m, 3 × CH_2 ring).

Compound (43): (9%) t.l.c. R_F 0.44 ($CHCl_3$); δ [by difference from major diastereoisomer of (42)] 4.80 (1 H, d, *J* 6 Hz, reduced to s on D_2O shake, C*H*OH), 3.30 (1 H, d, *J* 6 Hz, absent on D_2O shake, OH), 3.00—2.50 (3 H, m, CH_2CCl_2CH), and 2.50—1.50 (6 H, complex m, 3 × CH_2 ring).

2-*Phenylpropene* (α-*Methylstyrene*).—Standard reaction in CH_2Cl_2 for 1 h afforded 1,1,1-*trichloro*-4-*phenylpent*-4-*en*-2-*ol* (45) in 35% yield, b.p. 118—121 °C/0.3 mmHg after purification by pressure column chromatography ($CHCl_3$) (Found: C, 49.75; H, 4.15. $C_{11}H_{11}Cl_3O$ requires C, 49.43; H, 4.18%); t.l.c. R_F 0.45 ($CHCl_3$); $\nu_{max.}$ (film) 3 450, 3 080, 3 050, 3 020, 2 920, 1 900—1 700 (overtones), 1 630, 1 600, 1 575, 1 095, 895, 800, and 715 cm^{-1}; δ 7.50—7.20 (5 H, m, aryl H), 5.48 (1 H, br s, 5a-H), 5.30 (1 H, br s, 5b-H), 4.11 (1 H, ddd, separations 2, 5, and 10 Hz, reduced to dd on D_2O shake with loss of 5 Hz splitting, 2-H), 3.44 (1 H, dd, separations 2 and 14 Hz, 3a-H), 2.71 (1 H, dd, separations 10 and 14 Hz, 3b-H), and 2.71 (1 H, d, *J* 5 Hz, absent on D_2O shake, OH).

Isoprene.—Reaction conducted in the presence of 100 mol% Et_2AlCl in hexane–CH_2Cl_2 (Method 1) at −40 °C prior to the addition of the catalyst and then at −30 °C for a further 20 min before quenching, afforded a 75 : 25 mixture of the ene adduct 1,1,1-*trichloro*-4-*methylenehex*-5-*en*-2-*ol* (46) and 6-*trichloromethyl*-4-*methyloxacyclohex*-3-*ene* (47), formally a Diels–Alder adduct. The two products co-distilled (b.p. 58—60 °C/0.15 mmHg), but separation was achieved by pressure column chromatography ($CHCl_3$).

Compound (46): (22%), t.l.c. R_F 0.43 ($CHCl_3$); *m*/*z* ($M^{+\cdot}$) 213.9714 ($C_7H_9{}^{35}Cl_3O^{+\cdot}$ requires 213.9719); $n_D{}^{23}$ 1.5226; $\nu_{max.}$ (film) 3 450, 3 080, 2 930, 1 595, 1 090, 1 000, 915, 900, 820, and 770 cm^{-1}; δ 6.50 (1 H, dd, separations 11 and 17 Hz, 4-H), 5.50—5.15 (4 H, complex m, 2 × $=CH_2$), 4.27 (1 H, ddd, separations 2, 5, and 10 Hz, reduced to dd on D_2O shake with loss of 5 Hz splitting, 2-H), 3.17 (1 H, d, *J* 14 Hz, 3a-H), 2.78 (1 H, d, *J* 5 Hz, absent on D_2O shake, OH), and 2.50 (1 H, dd, separations 10 and 14 Hz, 3b-H).

Compound (47): (7.2%), t.l.c. R_F 0.80 ($CHCl_3$); *m*/*z* ($M^{+\cdot}$) 213.9725 ($C_7H_9{}^{35}Cl_3O^{+\cdot}$ requires 213.9719); $n_D{}^{23}$ 1.5083; $\nu_{max.}$ (film) 3 030, 2 920, 1 640, 1 140, 815, and 775 cm^{-1}; δ 5.54 (1 H, m, 3-H), 4.41 (2 H, m, 2 × 2-H), 4.05 (1 H, dd, separations 6 and 8 Hz, 6-H), 2.40 (2 H, m, 2 × 5-H), and 1.82 (3 H, br s, CH_3).

Reactions catalysed by $AlCl_3$ gave variable ratios of (46) : (47), but the ene adduct (46) was favoured by low $AlCl_3$ concentrations (*ca.* 1 mol%) and short contact times. The conversion of (46) into (47) in the presence of $AlCl_3$ (10 mol%) was followed by ^1H n.m.r.; reaction was complete in 2 h at room temperature.

Isopropenyl Acetate.—Reaction in CH_2Cl_2 in the presence of 20 mol% $AlCl_3$ for 4 days afforded a mixture of 1,1,1-*trichloro*-4-*oxopentan*-2-*yl acetate* (50), 5,5,5-*trichloro*-4-*acetoxypent*-1-*en*-2-*yl acetate* (51), 5,5,5-*trichloro*-4-*hydroxypentan*-2-*one* (52), and 5,5,5-*trichloropent*-3-*en*-2-*one* (53) in a ratio of 50 : 30 : 10 : 10 (*ca.* 60%). The four products were readily separated by pressure column chromatography (CH_2Cl_2). A reduction in catalyst concentration, but with the same reaction time, resulted in different product ratios (see Table 5), and compound (53) could no longer be detected. On the other hand, thermal addition under reduced pressure at 140 °C for 24 h afforded a 60 : 20 : 20 mixture (*ca.* 11%) of (50) : (51) : (53) with compound (52) absent.

Compound (50): b.p. 72—74 °C/0.6 mmHg (Found: C, 34.1; H, 3.8. $C_7H_9Cl_3O_3$ requires C, 33.97; H, 3.67%); t.l.c. R_F 0.24 (CH_2Cl_2); $\nu_{max.}$ (film) 2 950, 1 760, 1 720, 1 375, 1 210, 1 075, 800, and 765 cm^{-1}; δ 6.02 (1 H, dd, separations 3 and 8 Hz, 2-H), 3.28 (1 H, dd, separations 3 and 17 Hz, 3a-H), 3.02 (1 H, dd, separations 8 and 17 Hz, 3b-H), 2.24 (3 H, s, 3 × 5-H), and 2.15 (3 H, s, $OCOCH_3$); δ_C 202.15 (s, C-4), 168.55 (s, $OCOCH_3$), 99.53 (s, C-1), 76.75 (d, C-2), 30.17 (q, C-5), and 20.55 (q, $OCOCH_3$).

Compound (51): b.p. 80—82 °C/0.6 mmHg (Found: C,

37.0; H, 4.2. $C_9H_{11}Cl_3O_4$ requires C, 37.33; H, 3.83%), t.l.c. R_F 0.33 (CH_2Cl_2); $\nu_{max.}$ (film) 2 960, 1 760, 1 675, 1 375, 1 220, 1 200, 800, and 780 cm^{-1}; δ 5.62 (1 H, dd, separations 2 and 10 Hz, 4-H), 4.88 (1 H, *ca.* s, 1a-H), 4.84 (1 H, *ca.* s, 1b-H), 3.11 (1 H, br d, *J* 15 Hz, 3a-H), 2.70 (1 H, dd, separations 10 and 15 Hz, 3b-H), and 2.17 (6 H, s, 2 × CH_3); δ_C 169.10 (s, CO at C-2), 168.69 (s, CO at C-4), 149.99 (s, C-2), 105.15 (t, C-1), 99.24 (s, C-5), 77.66 (d, C-4), 35.73 (t, C-3), 21.05 (q, CH_3 at C-2), and 20.50 (q, CH_3 at C-4).

Compound (52): Kugelröhr distilled at 62 °C/0.5 mmHg, solidified to give colourless crystals, m.p. 74—75 °C (lit.,[17] m.p. 75—76 °C); t.l.c. R_F 0.05 (CH_2Cl_2), eluted from column using EtOH; $\nu_{max.}$ (KBr) 3 380, 2 900, 1 715, 1 115, 820, and 765 cm^{-1}; δ 4.60 (1 H, dd, separations *ca.* 3.5 and 8 Hz, 4-H), 4.08 (1 H, br s, absent on D_2O shake, OH), 3.20—2.72 (2 H, m, AB of ABX, separations *ca.* 3.5, 8, and 18 Hz, 2 × 3-H), and 2.26 (3 H, s, 3 × 1-H).

Compound (53): b.p. 90—92 °C/10 mmHg; t.l.c. R_F 0.50 (CH_2Cl_2); $\nu_{max.}$ (film) 3 030, 2 920, 1 705, 1 680, 1 625, 970, 775, and 730 cm^{-1}; δ 6.90 (1 H, d, *J* 15 Hz, 4-H), 6.48 (1 H, d, *J* 15 Hz, 3-H), and 2.36 (3 H, s, 3 × 1-H).

2-*Methoxypropene*.—(*a*) Reaction in the Carius tube equipped with a high vacuum Teflon screw valve, under air, at 120 °C for 24 h, afforded a complex mixture of products. The five major components were identified as 2,2,2-*trichloro*-1-*methoxyethanol* (54), 6-*trichloromethyl*-2,2-*dimethyloxacyclohexan*-4-*one* (55), 3,5,5-*trichloropent*-4-*en*-2-*one* (56), 1,5,5-*trichloropent*-4-*en*-2-*one* (57), and 5,5,5-*trichloro*-4-*hydroxypentan*-2-*one* (52); product ratio 27 : 27 : 13 : 13 : 20 (yield *ca.* 55%). Careful fractional distillation followed by pressure column chromatography (CH_2Cl_2) of the separate fractions enabled all five products to be isolated.

Compound (54): b.p. 55—57 °C/20 mmHg, solidified to give colourless crystals m.p. 49—50 °C (lit.,[18] m.p. 50 °C); $\nu_{max.}$ (KBr) 3 375, 2 940, 1 115, and 820 cm^{-1}; δ 4.76 (1 H, s, C*H*OH), 3.62 (3 H, s, OCH_3), and 2.60 (1 H, br s, absent on D_2O shake, OH).

Compound (55): m.p. 79.5—80 °C (Found: C, 39.45; H, 4.6. $C_8H_{11}Cl_3O_2$ requires C, 39.13; H, 4.52%); R_F 0.40 (CH_2Cl_2); $\nu_{max.}$ (KBr) 2 980, 1 715, 1 245, and 760 cm^{-1}; δ 4.36 (1 H, dd, separations 3.5 and 10.5 Hz, 6-H), 2.92 (1 H, dd, separations 3.5 and 14.5 Hz, 5a-H), 2.65 (1 H, dd, separations 10.5 and 14.5 Hz, 5b-H), 2.52 (1 H, highly perturbed d, A of AB, *J* 15 Hz, 3a-H), 2.42 (1 H, highly perturbed d, B of AB, *J* 15 Hz, 3b-H), 1.51 (3 H, s, CH_3), and 1.33 (3 H, s, CH_3); decoupling, irradiation at: δ 4.36 (reduces dd at 2.92 to d with loss of 3.5 Hz splitting; dd at 2.65 to d with loss of 10.5 Hz splitting; identifies separate CH_2 groups); δ_C 204.92 (s, C-4), 99.92 (s, CCl_3), 80.60 (d, C-6), 76.13 (s, C-2), 52.22 (t, C-5), 42.67 (t, C-3), 30.40 (q, CH_3), and 24.26 (q, CH_3).

Compound (56): b.p. 88—90 °C/15 mmHg (Found: C, 32.35; H, 2.8. $C_5H_5Cl_3O$ requires C, 32.04; H, 2.69%); t.l.c, R_F 0.63 (CH_2Cl_2); $\nu_{max.}$ (film) 3 050, 2 950, 1 720, 1 615, 920. 855, and 800 cm^{-1}; δ 6.23 (1 H, d, *J* 10 Hz, 4-H), 5.10 (1 H, d, *J* 10 Hz, 3-H), and 2.40 (3 H, s, 3 × 1-H); δ_C 197.89 (s, C-2), 128.08 (s, C-5), 123.82 (d, C-4), 58.78 (d, C-3), and 26.58 (q, C-1).

Compound (57): Kugelröhr distilled at 75 °C/2 mmHg; *m/z* ($M^{+\cdot}$) 185.9412 ($C_5H_5{}^{35}Cl_3O^{+\cdot}$ requires 185.9406); t.l.c. R_F 0.53 (CH_2Cl_2); $\nu_{max.}$ (film) 3 050, 2 930, 1 735, 1 625, 920, 890, and 780 cm^{-1}; δ 6.20 (1 H, t, *J* 7 Hz, 4-H), 4.17 (2 H, s, 2 × 1-H), and 3.57 (2 H, d, *J* 7 Hz, 2 × 3-H); δ_C 198.04 (s, C-2), 124.03 (s, C-5), 120.88 (d, C-4), 47.75 (t, C-1), and 40.20 (t, C-3).

(*b*) Reaction in CH_2Cl_2 in the presence of either 2 mol% or 10 mol% $AlCl_3$, for 1.5 h and 3 days respectively, afforded only compound (54).

(*c*) Reaction in the presence of 100 mol% Et_2AlCl in hexane–CH_2Cl_2 (Method 1) with the reagent mixture cooled to −40 °C prior to addition of the catalyst, and then maintained at −20 to −30 °C for a further 2 h before quenching at below 0 °C, afforded a complex mixture of products. Pressure column chromatography (CH_2Cl_2 to R_F 0.2 followed by CH_2Cl_2–EtOAc, 4 : 1, v/v), gave (55) and the major component, isolated as a light brown oil, which was identified as 1,1,1,7,7,7-*hexachloro*-2,6-*dihydroxyheptan*-2-*one* (60). Impure (60) solidified with time and was washed with pentane and then recrystallized from hexane–$CHCl_3$ (9 : 1, v/v) to give colourless crystalline material (11%), m.p. 126—128 °C (lit.,[19] m.p. 124—126 °C) (Found: C, 24.2; H, 2.4. $C_7H_8Cl_6O_3$ requires C, 23.83; H, 2.29%); t.l.c. R_F 0.60 (CH_2Cl_2–EtOAc, 4 : 1, v/v); $\nu_{max.}$ (KBr) 3 400, 2 900, 1 700, 1 100, 815, 790, and 760 cm^{-1}; δ 4.74 (2 H, m, reduced to dd on D_2O shake, separations *ca.* 3 and 8 Hz, 2-H + 6-H), 3.45 (2 H, br s, absent on D_2O shake, OH), 3.34—2.85 (4 H, overlapping t and q, separations *ca.* 3, 8, and 17 Hz, 2 × 3-H + 2 × 5-H); δ_C 203.86 (s, C-4), 102.24 (s, C-1 + C-7), 79.01 (d, C-2 + C-6), and 45.90 (t, C-3 + C-5).

2-*Bromopropene*.—Reaction in CCl_4 in the presence of 2 mol% $AlCl_3$ for 18 h followed by pressure column chromatography of the oily residue afforded the ene adduct (61) and crystalline 4-*bromo*-1,1,1,4-*tetrachloropentan*-2-*ol* (62). The adduct (61), 4-*bromo*-1,1,1-*trichloropent*-4-*en*-2-*ol*, crystallized with time to a waxy solid.

Compound (61): (29%), b.p. 72—75 °C/0.06 mmHg, m.p. 49—50 °C; t.l.c. R_F 0.37 (C_6H_6) (Found: C, 22.95; H, 2.4. $C_5H_6BrCl_3O$ requires C, 22.37; H, 2.40%); $\nu_{max.}$ (film) 3 420, 3 080, 2 900, 1 625, 1 275, 1 200, 1 130, 1 090, 990, 900, 820, and 795 cm^{-1}; δ 5.82 (1 H, s, 5a-H), 5.62 (1 H, s, 5b-H), 4.40 (1 H, br d, separation 9 Hz, reduces to dd on D_2O shake, separations 2 and 9 Hz, 2-H), 3.42 (1 H, br d, *J* 4 Hz, absent on D_2O shake, OH), 3.14 (1 H, br d, *J* 16 Hz, 3a-H), and 2.76 (1 H, dd, separations 9 and 16 Hz, 3b-H); δ_C 127.95 (s, C-4), 120.99 (t, C-5), 102.45 (s, C-1), 80.29 (d, C-2), and 43.74 (t, C-3).

Compound (62): (5.5%), m.p. 57—59 °C; t.l.c. R_F 0.50 (C_6H_6); $\nu_{max.}$ (KBr) 3 490, 2 980, 2 910, 1 390, 1 325, 1 295, 1 220, 1 175, 1 115, 1 075, 875, 830, 790, and 695 cm^{-1}; δ 4.45 (1 H, br d, *J* 8 Hz; *ca.* dq, J_1 *ca.* 1 Hz, J_2 8 Hz, after D_2O shake, 2-H), 3.37 (1 H, br s, absent on D_2O shake, OH), 3.20 (1 H, m approx. to pentet, separations *ca.* 8 Hz, 3a-H), 2.90—2.28 (1 H, partly obscured m, 3b-H), 2.68 and 2.50 (total 3 H, s and d respectively, *J* 2 Hz, CH_3 of diastereoisomers); diastereoisomeric ratio *ca.* 2 : 1.

cis- *and* trans-1-*Bromopropene*.—The commercially available olefin, comprising a mixture of geometric isomers, was treated with chloral in CCl_4 in the presence of 6 mol% $AlCl_3$ for 48 h. The recovered olefin contained more of the *trans*-isomer than the starting material, implying preferential reaction of the *cis*-olefin or *cis*/*trans* isomerization under the reaction conditions. The crude product after work-up exhibited a very complex ^1H n.m.r. spectrum, which was to be expected in view of the four diastereoisomeric modifications for the ene adduct and ketonic product alone. Treatment with pyridine and pressure column chromatography (C_6H_6) afforded two main fractions, one containing the ene adduct 3-bromo-1,1,1-trichloropent-4-en-2-ol and the other containing *E*- and *Z*-3-bromo-1,1-dichloropent-3-en-2-one, mixtures (X) and (Y) respectively.

Mixture (X): (11%), b.p. 103—105 °C/3 mmHg; t.l.c. R_F 0.43 (C_6H_6); $\nu_{max.}$ (film) 3 440, 3 020, 2 930, 2 880, 1 620—1 600br, 1 385, 1 250, 1 110, 925, 830, and 790 cm^{-1}; δ 5.10 (d, 3 Hz, CHBr), 4.92—4.36 (complex m, olefinic H and C*H*OH), 3.32 (br s, absent on D_2O shake, OH); the probable

presence of the hydrochlorinated ene adduct (four possible diastereoisomers) was indicated by multiple peaks at δ 1.76—1.36 (CH_3).

Mixture (Y): (7%), b.p. 75—77 °C/4 mmHg; t.l.c. R_F 0.53 (C_6H_6); $\nu_{max.}$ (film) 2 950, 2 880, 1 695, 1 605, and 810 cm^{-1}; δ 7.66 and 7.44 (overlapping q, *J* 7 Hz, $CH_2CH=$), 6.78 and 6.76 (two s, $COCHCl_2$), and 2.12 and 2.10 (two d, *J* 7 Hz, CH_3CH).

Addition Reactions with Bromal

The reactions of bromal were uniformly slower than the corresponding chloral additions. The spectroscopic properties of the reaction products (ene adducts, ketones, or hydrohalogenated derivatives) were closely similar to the structurally related chloral products, the main differences being: $\nu_{max.}$ absorptions near 750 and 725 cm^{-1} (C–Br stretch); δ resonances near 3.9 ($CHOH{\cdot}CBr_3$), 5.8 ($COCHBr_2$), and 4.4 (CHBr); δ_C resonances near 83 ($CHOH{\cdot}CBr_3$), 54 (CBr_3), 48 ($COCHBr_2$), and 42 (CHBr). Accordingly, spectroscopic details are given only when the bromal product does not correspond simply with one of the above-mentioned chloral addition products.

The bromal adducts were generally much more labile than the analogous chloral products, and short path-length distillations under reduced pressure were essential.

(−)-β-*Pinene*.—(*a*) Reaction in CCl_4 in the presence of 2 mol% $AlCl_3$ for 3—6 h afforded 1,1,1-*tribromo*-3-{(1S,5S)-6,6-*dimethylbicyclo*[3.1.1]*hept*-2-*en*-2-*yl*}*propan*-2-*ol* (1b) in 70% yield, b.p. 100—105 °C/0.1 mmHg (Found: C, 34.7; H, 4.4; Br, 59.75. $C_{12}H_{17}Br_3O$ requires C, 34.57; H, 4.11; Br, 59.49%); t.l.c. R_F 0.49 ($CHCl_3$). The product was a 75 : 25 mixture of diastereoisomers; the isomer ratio depended upon the Lewis acid catalyst. The ene adduct (1b) was obtained as a solid, m.p. 54—56.5 °C, in the thermally initiated reaction (mainly 11*R*-isomer), and also in the $FeCl_3$-catalysed reaction, m.p. 60—62 °C (mainly 11*S*-isomer). Details of this stereoselectivity are given in the following paper.[5a]

(*b*) Reaction of bromal with an equimolar quantity of (−)-β-pinene at 46 °C for 8 days in a sealed tube in the dark afforded a black viscous oil. The oil was taken up in *ca.* twice its volume of CCl_4 and the organic liquors stirred with an equal volume of 2M-sulphuric acid for 1 h. The organic phase was then washed with saturated aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). Filtration and removal of the solvent gave a brown oil which was purified by pressure column chromatography (C_6H_6) to give the ene adduct (1b) as a white solid, m.p. 54—56.5 °C in 21% yield.

(*c*) A solution of bromal (7.0 g, 25 mmol) and β-pinene (3.4 g, 25 mmol) in light petroleum (b.p. 40—60 °C) (15 ml) was boiled under gentle reflux for 12 days under normal laboratory lighting. On cooling and standing overnight, colourless needle-like crystals, m.p. 62—64 °C, were formed (6.25 g, 60%). This compound was identified as the radical-derived aldehyde 3-{4-(2-*bromopropan*-2-*yl*)*cyclohex*-1-*enyl*}-2,2-*dibromopropanal* (2b), $[\alpha]_D^{24}$ −65° (*c*, 0.0783), t.l.c. R_F 0.58 (C_6H_6); $\nu_{max.}$ (KBr) 2 930, 1 725, 1 430, 1 370, 1 105, and 990 cm^{-1}; δ 8.24 (1 H, s, CHO), 5.72 (1 H, br s, olefinic H), 3.21 (2 H, s, CH_2CBr_2), 2.50—1.44 (7 H, m, ring CH and CH_2), 1.80 (3 H, s, CH_3), and 1.74 (3 H, s, CH_3); δ_C 183.65 (d, CHO), 132.10 (s, $CH=C$), 128.71 (d, $CH=C$), 72.28 (s, CBr_2), 69.56 (d, $CHCBrMe_2$), 49.12 (t, CH_2CBr_2), 46.72 (s, $CBrMe_2$), 32.63 (q, CH_3), 31.40 (q, CH_3), 30.64 (t, allylic ring CH_2), 28.42 (t, allylic ring CH_2), and 25.85 (t, non-allylic ring CH_2).

Use of radical initiators (dibenzoyl peroxide, azobisisobutyronitrile, *etc.*), or visible or u.v. radiation, increased the rate of reaction of bromal but gave tarry products from which much smaller quantities of (2b) could be isolated.

2-*Methylpropene*.—The adduct, 1,1,1-*tribromo*-4-*methylpent*-4-*en*-2-*ol* (5b) was obtained as a yellow solid; crystallisation from light petroleum (b.p. 40—60 °C) gave colourless needles, m.p. 61—62 °C (64%), t.l.c. R_F 0.33 (C_6H_6) (Found: C, 21.4; H, 3.1. $C_6H_9Br_3O$ requires C, 21.39; H, 3.69%); δ_C 140.76 (s, C-4), 114.34 (t, C-5), 82.22 (d, C-2), 54.27 (s, C-1), 41.40 (t, C-3), and 22.46 (q, CH_3).

Hydrogenation of (5b) at room temperature and atmospheric pressure in EtOAc in the presence of Adams catalyst ceased when the theoretical quantity of H_2 for saturation of the C=C had been absorbed. Conventional work-up afforded 1,1,1-*tribromo*-4-*methylpentan*-2-*ol*, a white crystalline solid m.p. 55—57 °C [from light petroleum (b.p. 40—60 °C)]; t.l.c. R_F 0.38 (C_6H_6) (Found: C, 21.15; H, 3.3; Br, 70.7. $C_6H_{11}Br_3O$ requires C, 21.27; H, 3.27; Br, 70.74%); $\nu_{max.}$ (KBr) 3 350, 2 940, 1 470, 1 390, 1 135, 1 010, 745, and 700 cm^{-1}; δ 3.98 (1 H, dd, separations 2 and 9 Hz, 2-H), 3.20 (1 H, s, absent on D_2O shake, OH), 2.08—1.54 (3 H, m, 2 × 3-H + 4-H), and 1.06 (6 H, d, *J* 5 Hz, 2 × CH_3).

2-*Methylbut*-1-*ene*.—Reaction afforded a mixture of 1,1,1-*tribromo*-4-*methylenehexan*-2-*ol* (6b) and cis- and trans-1,1,1-*tribromo*-4-*methylhex*-4-*en*-2-*ol* (7b) in a *ca.* 25 : 75 ratio (43%), b.p. 81—82 °C/0.09 mmHg. The three compounds were unresolved on chromatography (R_F 0.37—0.44, C_6H_6), and the physical data refers to the mixture (Found: C, 23.85; H, 3.4; Br, 67.7. $C_7H_{11}Br_3O$ requires C, 23.96; H, 3.16; Br, 68.32%); $\nu_{max.}$ (film) 3 450, 2 950, 2 900, 1 660, 1 640, 1 440, 1 380, 1 275, 1 080, 745, and 695 cm^{-1}; δ 5.48 (1 H, br q, $=CHCH_3$), 4.97 (2 H, br s, $=CH_2$), 4.03 (1 H, m, sharpened on D_2O shake, $CHOH$ all isomers), 3.16 (1 H, br s, absent on D_2O shake, OH all isomers), 3.10—2.05 (2 H, complex m, CH_2 all isomers), 1.76 (3 H, m, $=CHCH_3$ both isomers), and 1.10 (3 H, t, *J* 7 Hz, CH_2CH_3). Integrated peak areas of the signals for isomers (6b) and (7b) gave a product ratio of *ca.* 25 : 75.

Methylenecyclopentane.—The ene adduct solidified, and recrystallization from light petroleum (b.p. 40—60 °C) and sublimation *in vacuo* afforded white needles, m.p. 68.5—70 °C, of 1-(1,1,1-*tribromo*-2-*hydroxypropan*-3-*yl*)*cyclopentene* (8b) (48%), t.l.c. R_F 0.38 (C_6H_6) (Found: C, 26.4; H, 2.95. $C_8H_{11}Br_3O$ requires C, 26.48; H, 3.06%).

(+)-*Limonene*.—Reaction was unusually slow, and freshly purified olefin was therefore employed; nonetheless, reaction in CH_2Cl_2 in the presence of 6 mol% $AlCl_3$ still required 22—24 h for completion. The viscous dark oily product (74%) showed appreciable decomposition upon distillation under reduced pressure on account of its high b.p., hence purification was effected by pressure column chromatography ($CHCl_3$). Three main fractions were obtained; the first (R_F 0.73) proved to be recovered limonene (27%), the second fraction (R_F 0.41) was identified as the *ene adduct* (9b) (20%), and the third fraction (R_F 0.36) gave an ill-defined ^1H n.m.r. spectrum, possibly indicating the presence of a mixture (18%) of the isomeric adducts (10b) and the bromine analogue of (10c). The ^1H n.m.r. spectrum for (9b) was similar, but with appropriate upfield shifts, to the spectrum detailed for the chloral adduct (9a). Comparison of the ^1H n.m.r. signals for the distilled crude adduct mixture at δ 1.76 and 1.68 indicated a (9b) : (10b) + (10c) ratio of *ca.* 2 : 1. We do not place reliance in this result, however, because of lack of positive identification of all the isomers and problems concerning thermal decomposition during distillation, unlike the chloral case.

2-*Methylbut*-2-*ene*.—Reaction afforded a 75 : 25 mixture (25%) of the ene adduct 1,1,1-*tribromo*-3,4-*dimethylpent*-4-*en*-2-*ol* (12b) and hydrohalogenated adduct 1,1,1,4-*tetrabromo*-3,4-*dimethylpentan*-2-*ol* (13b). Analysis of the ^{1}H n.m.r. spectra indicated that each compound comprised an 85 : 15 mixture of diastereoisomers.

Compound (12b): (18%), b.p. 100—103 °C/0.7 mmHg, solidified with time and formed colourless platelets, m.p. 58.5—59.5 °C, after repeated recrystallization from light petroleum (b.p. 40—60 °C) (Found: C, 24.05; H, 3.25. $C_7H_{11}Br_3O$ requires C, 23.96; H, 3.16%). Recrystallization removed the minor diastereoisomer; t.l.c. R_F (minor diastereoisomer; *R*,*R* + *S*,*S*) 0.47 and (major diastereoisomer; *R*,*S* + *S*,*R*) 0.43 ($CHCl_3$). Stereochemical assignments are based on spectroscopic comparisons with the chloral ene adduct (12a) the configuration of which has been established by *X*-ray methods.[5a] Estimation of the diastereoisomeric composition was carried out on the *unfractionated* mixture of isomers from an inspection of the ^{1}H n.m.r. integrals: δ 4.75 (2 H, m, 2 × 5-H), 4.00 (0.85 H, br s, forms sharp d on D_2O shake, *J* 2.5 Hz, 2-H of major isomer), 3.80 (0.15 H, br s, forms sharp d on D_2O shake, *J* 4 Hz, 2-H of minor isomer), 2.91 (1 H, br s, absent on D_2O shake, OH), 2.90 (1 H, qd, separations 2.5 and 7 Hz, 3-H), 1.80 (3 H, s, CH_3 at C-4), 1.27 (0.45 H, d, *J* 7 Hz, CH_3 at C-3 of minor isomer), and 1.23 (2.55 H, d, *J* 7 Hz, CH_3 at C-3 of major isomer).

Compound (13b): predominant compound in the higher boiling distillation fraction, b.p. 106—112 °C/0.7 mmHg; t.l.c. R_F 0.47 and 0.43 ($CHCl_3$), two diastereoisomers; δ [by difference from (12b)] 4.40 (1 H, br s, 2-H), 2.55 (1 H, m, 3-H), 1.67 [*ca.* 2.55 H, s, C*H*$_3$C(CH$_3$)Cl, major diastereoisomer], 1.59 [*ca.* 2.55 H, s, CH$_3$C(C*H*$_3$)Cl, major diastereoisomer], 1.50 [*ca.* 0.45 H, s, C*H*$_3$C(CH$_3$)Cl, minor isomer], 1.41 [*ca.* 0.45 H, s, CH$_3$C(C*H*$_3$)Cl, minor isomer], the other signals were obscured by those for (12b).

Propene.—(*a*) Treatment of the crude reaction product with pyridine followed by pressure column chromatography (C_6H_6) afforded 1,1,1-*tribromopent*-4-*en*-2-*ol* (24b) (10%), and 1,1-*dibromopent*-3-*en*-2-*one* [(25b) − HBr] (63%).

Compound (24b): b.p. 62—66 °C/0.3 mmHg; t.l.c. R_F 0.32 (C_6H_6) (Found: C, 18.5; H, 2.4. $C_5H_7Br_3O$ requires C, 18.60; H, 2.19%); δ_C 132.80 (d, C-4), 118.18 (t, C-5), 83.10 (d, C-2), 54.27 (s, C-1), and 36.96 (t, C-3).

Compound [(25b] − HBr]: b.p. 52—56 °C/0.3 mmHg; t.l.c. R_F 0.58 (C_6H_6) (Found: C, 24.5; H, 2.5; Br, 65.1. $C_5H_6Br_2O$ requires C, 24.83; H, 2.50; Br, 66.06%); $\nu_{max.}$ 2 935, 1 680, 1 620, 1 335, 1 285, 1 155, and 985 cm^{-1}; δ 7.29 (1 H, dq, separations 7 and 17 Hz, 4-H), 6.69 (1 H, d, *J* 17 Hz, 3-H), 5.99 (1 H, s, 1-H), and 2.28 (3 H, d, *J* 7 Hz, 3 × 5-H).

(*b*) Distillation of the crude product after the addition reaction (*i.e.* excluding the pyridine treatment) afforded a 1 : 6 mixture of (24b) and (25b) with traces of [(25b) − HBr], 96% total yield. A small sample of pure 1,1,4-*tribromopentan*-2-*one* (25b) was isolated by g.l.c. on a small scale using an analytical scale g.l.c. column; bulk separation of (24b) and (25b) is best achieved by chromatography over 100—200 mesh silica gel using gravity flow.

Compound (25b): b.p. 62—66 °C/0.3 mmHg; t.l.c. R_F 0.54 (C_6H_6); $\nu_{max.}$ (film) 3 000, 1 730, 1 455, 1 390, 1 250, 1 140, and 1 005 cm^{-1}; δ 5.83 (1 H, s, 1-H), 4.52 (1 H, *ca.* sextet, separations *ca.* 8 Hz, 4-H), 3.52 (2 H, two dd overlapping to give symm. seven peaks, AB of ABX spin system, separations 8 and 16 Hz for both dd, 2 × 3-H), and 1.79 (3 H, d, *J* 6.6 Hz, 3× 5-H); spin decoupling with irradiation at δ 1.79 reduced the 4.52 signal to an unsymmetrical t (*J* 7—8 Hz); δ_C 192.28 (s, C-2), 45.62 (t, C-3), 42.34 (d, C-1), 41.99 (d, C-4), and 25.61 (q, C-5).

But-1-*ene*.—Reaction was followed first by treatment of the crude product with pyridine and then pressure column chromatography (C_6H_6) to give the ene adduct 1,1,1-*tribromohex*-4-*en*-2-*ol* (24c) and the enone 1,1-*dibromohex*-3-*en*-2-*one* [(25c) − HBr].

Compound (24c): (30%), b.p. 105—108 °C/0.5 mmHg; t.l.c. R_F 0.34 (C_6H_6) (Found: C, 21.75; H, 2.75; Br, 70.35. $C_6H_9Br_3O$ requires C, 21.39; H, 2.69; Br, 71.16%); $\nu_{max.}$ (film) 3 400, 2 950, 2 890, 1 425, 1 370, 1 270, 1 060, 965, 740, and 705 cm^{-1}; δ 5.76 (2 H, m, 4-H + 5-H), 4.01 (1 H, dd, separations 2 and 9 Hz, 2-H), 3.15 (1 H, br s, absent on D_2O shake, OH), 2.98 (1 H, br d, *J* 12 Hz, 3a-H), 2.39 (1 H, br m, 3b-H), and 1.18 (3 H, d, *J* 5 Hz, 3 × 6-H).

Compound [(25c) − HBr]: (24%), b.p. 52 °C/0.05 mmHg; t.l.c. R_F 0.60 (C_6H_6) (Found: C, 28.3; H, 3.15. $C_6H_8Br_2O$ requires C, 28.16; H, 3.15%); $\nu_{max.}$ (film) 2 940, 1 680, 1 620 1 335, 1 290, 1 155, and 985 cm^{-1}; δ 7.32 (1 H, dt, separations 6 and 16 Hz, 4-H), 6.71 (1 H, d, *J* 16 Hz, 3-H), 5.99 (1 H, s, 1-H), 2.42 (2 H, m, 2 × 5-H), and 1.18 (3 H, t, *J* 9 Hz, 3 × 6-H).

Hex-1-*ene*.—Reaction followed by treatment with pyridine and then pressure column chromatography (C_6H_6) afforded the ene adduct 1,1,1-*tribromo*-*oct*-4-*en*-2-*ol* (24e) and the enone 1,1-*dibromo*-*oct*-3-*en*-2-*one* [(25e) − HBr]. Conversely, reaction followed by chromatography of the oily residue over 100—200 mesh silica gel (C_6H_6) using gravity flow afforded (24e) and the tribromo ketone 1,1,4-*tribromo*-*octan*-2-*one* (25e).

Compound (24e): (40%), b.p. 60—64 °C/0.01 mmHg; t.l.c. R_F 0.40 (C_6H_6) (Found: 26.1; H, 4.2; Br, 65.35. $C_8H_{13}Br_3O$ requires C, 26.33; H, 3.59; Br, 65.69%).

Compound (25e): (20%), b.p. 60—61 °C/0.01 mmHg; t.l.c. R_F 0.56 (C_6H_6); δ_C 192.57 (s, C-2), 48.48 (d, C-1), 44.27 (t, C-3), 42.57 (d, C-4), 37.95 (t, C-5), 29.36 (t, C-6), 21.81 (t, C-7), and 13.86 (q, C-8); δ 5.79 (1 H, s, 1-H), 4.32 (1 H, br pentet, separations *ca.* 7 Hz, 4-H), 3.47 (2 H, two overlapping dd, separations both 7 and 18 Hz, 2 × 3-H), 1.85 (2 H, m, 2 × 5-H), 1.45 (4 H, m, 2 × 6-H + 2 × 7-H), and 0.93 (3 H, t, *J* 8 Hz, 3 × 8-H); spin decoupling with irradiation at δ 1.85 reduced the signal at 4.32 to a t, and irradiation at δ 4.32 reduced the signal at 1.85 to a t and the signal at 3.47 to a d. These results uniquely define the position of attachment of Br at C-4.

Compound [(25e) − HBr]: (28%), b.p. 60—62 °C/0.01 mmHg; t.l.c. R_F 0.60 (C_6H_6) (Found: C, 33.55; H, 4.7. $C_8H_{12}Br_2O$ requires C, 33.83; H, 4.26%).

Hept-1-*ene*.—Reaction followed by treatment with pyridine and then pressure column chromatography (C_6H_6) afforded the ene adduct 1,1,1-*tribromonon*-4-*en*-2-*ol* (24f) and the enone 1,1-*dibromonon*-3-*en*-2-*one* [(25f) − HBr].

Compound (24f): (48%), b.p. 70—72 °C/0.02 mmHg; t.l.c. R_F 0.47 (C_6H_6) (Found: C, 28.9; H, 4.1; Br, 62.65. $C_9H_{15}Br_3O$ requires C, 28.53; H, 3.99; Br, 63.26%); $\nu_{max.}$ (film) 3 410, 3 000, 2 900, 2 840, 1 460, 1 430, 1 075, 975, 745, and 710 cm^{-1}; δ 5.5 (2 H, m, 4-H + 5-H), 3.86 (1 H, dd, separations 2 and 9 Hz, 2-H), 3.04 (1 H, br s, absent on D_2O shake, OH), 2.88 (1 H, br d, *J* 12 Hz, 3a-H), 2.22 (1 H, m, 3b-H), 2.00 (2 H, m, 2 × 6-H), 1.32 (4 H, m, 2 × 7-H + 2 × 8-H), and 0.92 (3 H, t, *J* 5 Hz, 3 × 9-H).

Compound [(25f) − HBr]: (32%), b.p. 67—69 °C/0.02 mmHg; t.l.c. R_F 0.63 (C_6H_6) (Found: C, 36.05; H, 4.4; Br, 54.05. $C_9H_{14}Br_2O$ requires C, 36.05; H, 4.73; Br, 53.62%); $\nu_{max.}$ (film) 2 900, 2 820, 1 680, 1 620, 1 465, and 1 145 cm^{-1};

δ 7.08 (1 H, dt, separations 6 and 16 Hz, 4-H), 6.51 (1 H, d, *J* 16 Hz, 3-H), 5.80 (1 H, s, 1-H), 2.30 (2 H, m, 2 × 5-H), 1.38 (6 H, br m, 2 × 6-H + 2 × 7-H + 2 × 8-H), and 0.93 (3 H, t, *J* 4 Hz, 3 × 9-H).

Oct-1-ene.—Reaction followed by treatment with pyridine and then pressure column chromatography (C_6H_6) afforded the ene adduct 1,1,1-*tribromodec-4-en-2-ol* (24h) and enone 1,1-*dibromodec-3-en-2-one* [(25h) − HBr].

Compound (24h): (49%), b.p. 80—86 °C/0.02 mmHg; t.l.c. R_F 0.48 (C_6H_6) (Found: C, 30.7; H, 4.3; Br, 59.65. $C_{10}H_{17}Br_3O$ requires C, 30.57; H, 4.36; Br, 61.00%).

Compound [(25h) − HBr]: (34%), b.p. 72—74 °C/0.02 mmHg; t.l.c. R_F 0.61 (C_6H_6) (Found: C, 38.42; H, 5.06. $C_{10}H_{16}Br_2O$ requires C, 38.49; H, 5.17%); $\nu_{max.}$ (film) 2 895, 2 810, 1 680, 1 620, 1 525, 1 460, 1 445, and 970 cm^{-1}; δ 7.04 (1 H, dt, separations 7 and 16 Hz, 4-H), 6.46 (1 H, d, *J* 16 Hz, 3-H), 5.80 (1 H, s, 1-H), 2.28 (2 H, br m, 2 × 5-H), 1.30 (8 H, br m, 4 × CH_2), and 0.90 (3 H, t, *J* 6 Hz, CH_3).

cis- *and* trans-*But-2-ene.*—Reactions were performed in CCl_4 solution in a manner similar to the chloral additions to these olefins. The additions essentially failed at the 2 and 6 mol% $AlCl_3$ catalyst levels. In the presence of 10 mol% $AlCl_3$ an exothermic reaction occurred and the reaction mixture turned a dark brown colour over the reaction time of 24 h. Work-up afforded a thick dark brown oil (*ca.* 65%); t.l.c. analysis (C_6H_6) showed the presence of several components, R_F 0.60, 0.39, 0.30, and 0.15—0.0 (streak). The i.r. spectrum of the crude product from the *cis*-but-2-ene reaction exhibited absorptions at $\nu_{max.}$ 3 550, 3 050, 2 970, 2 850, 1 730, 1 640, 1 450, 1 380, 1 050, 780, and 750 cm^{-1}; however, both the 3 550 and 1 730 cm^{-1} absorptions could be assigned to unchanged bromal and its hydrate. The crude product was distilled under reduced pressure at 0.01 mmHg and four dark brown fractions were collected, b.p. 38—76, 76—96, 96—98, and 115—130 °C (*ca.* 1 : 5 : 2.5 : 3 by weight). The i.r. spectra of each of these fractions were similar and the ^1H n.m.r. spectra were complex. Although the ene adduct was probably present it could not be isolated in a pure state for positive identification. Additionally, with catalyst levels in the range 6—20 mol%, large amounts of a flocculent white polymeric precipitate was obtained. The *trans*-but-2-ene/bromal reaction afforded similar results.

Cyclohexene.—Reaction in CH_2Cl_2 followed by pressure column chromatography (C_6H_6) afforded the ene adduct 2,2,2-*tribromo*-1-(*cyclohex-2-enyl*)*ethanol* (39d) and an ether which, by analogy with the chloral/cyclohexene reaction,[9] is assigned the structure 7-*tribromomethyl*-6-*oxabicyclo*[3.2.1]-*octane*. The ketonic compound (40d) was also detected in the crude product as a contaminant.

Compound (39d): (7%), m.p. 62—63 °C; t.l.c. R_F 0.42 (C_6H_6) (Found: C, 26.95; H, 2.98; Br, 65.51. $C_8H_{11}Br_3O$ requires C, 26.48; H, 3.06; Br, 66.06%); $\nu_{max.}$ (KBr) 3 430, 2 990, 2 860, 1 630, 1 440, 1 330, 1 320, 1 215, 1 125, 1 095, 895, 740, and 715 cm^{-1}; δ 6.16 (2 H, br s, olefinic H), 4.02 (1 H, br s, sharpened to a less br s on D_2O shake, C*H*OH), 3.08 (2 H, br m, reduces to 1 H, br m, on D_2O shake, OH + C*H*CHOH), 2.11 (2 H, br m, allylic CH_2 ring), and 1.82 (4 H, br m, non-allylic CH_2 ring). It was not apparent from the ^1H n.m.r. spectrum if the two diastereoisomeric modifications of (39d) were present but in view of the fact that (39d) was a solid it seems likely that the other (minor?) diastereoisomer was removed in the purification of the above compound.

The *cyclic ether:* (29%), b.p. 56—60 °C/0.2 mmHg; t.l.c. R_F 0.68 (C_6H_6) (Found: C, 26.8; H, 2.75. $C_8H_{11}Br_3O$ requires C, 26.48; H, 3.06%); $\nu_{max.}$ (film) 2 910, 2 850, 1 445, 1 335, 1 270, 1 175, 1 000, 975, 810, 740, 690, and 645 cm^{-1}; δ 4.5 and 4.25 (total 2 H, br overlapping m, intensity ratio 1 : 7, 5-H + 7-H), 2.36 (2 H, br m, 1-H + 8b-H), and 2.1—1.2 (7 H, br m, 8a-H + 3 × CH_2).

Cycloheptene.—Reaction in CH_2Cl_2 followed by pressure column chromatography (C_6H_6) of the oily residue afforded the ene adduct 2,2,2-*tribromo*-1-(*cyclohept-2-enyl*)*ethanol* (39f), the dehydrobrominated ketone, *dibromomethyl cyclohept-1-enyl ketone* [(40f) − HBr], and a cyclic ether assumed to be predominantly exo-8-*tribromomethyl*-7-*oxabicyclo*[4.2.1]-*nonane* by analogy with the results of our previous work on the chloral/cyclohexene reaction.[9]

Compound (39f): (8.2%), b.p. 93—96 °C/0.5 mmHg; t.l.c. R_F 0.45 (C_6H_6) (Found: C, 29.0; H, 3.95. $C_9H_{13}Br_3O$ requires C, 28.68; H, 3.78%); $\nu_{max.}$ (film) 3 400, 3 040, 2 900, 2 850, 1 635w, 1 440, 1 370, 1 215, 1 095, 1 005, 955, 925, 740, and 695 cm^{-1}; δ 4.96 (2 H, m, olefinic H), 4.58 (1 H, d, *J* 7 Hz, 1-H), 4.24 (d, *J* 5 Hz, probably 1-H of minor diastereoisomer), 2.91 (2 H, complex m, HC*H*CH=CHC*H*CHOH), 1.98 (6 H, complex m, ring CH + OH), and 1.26 (2 H, complex m, ring CH).

Compound [(40f) − HBr]: (7%), b.p. 82—86 °C/0.5 mmHg; t.l.c. R_F 0.65 (C_6H_6); $\nu_{max.}$ (film) 2 920, 2 850, 1 670, 1 620, 1 450, 1 155, 1 070, 915, 725, and 695 cm^{-1}; δ 7.30 (1 H, t, *J* 7 Hz, CH=C), 6.70 (1 H, s, $CHBr_2$), 2.55 (4 H, m, allylic CH_2 ring), and 1.78 (6 H, br m, non-allylic CH_2 ring).

8-*Tribromomethyl*-7-*oxabicyclo*[4.2.1]*nonane:* (8.5%), b.p. 80—84 °C/0.5 mmHg; t.l.c. R_F 0.73 (C_6H_6) (Found: C, 28.45; H, 3.55. $C_9H_{13}Br_3O$ requires C, 28.68; H, 3.78%); $\nu_{max.}$ (film) 2 900, 1 450, 1 160br, 1 070, 1 005, 950, and 655 cm^{-1}; δ 4.76 and 4.56 (total 2 H, sharp m, area ratio 1 : 3, 6-H + 8-H, possibly both *exo-* and *endo*-isomers), and 2.5—1.6 (11 H, complex br m, ring CH_2 + 1-H).

Cyclo-octene.—Reaction in CCl_4 followed by pressure column chromatography of the oily residue (C_6H_6) afforded the ene adduct 2,2,2-*tribromo*-1-(*cyclo-oct-2-enyl*)*ethanol* (39h) and an ether which, in view of the chloral/cyclohexene result,[9] was assigned the structure 9-*tribromomethyl*-8-*oxabicyclo*[5.2.1]*decane* or an isomer.

Compound (39h): (22%), b.p. 100—106 °C/0.6 mmHg; t.l.c. R_F 0.52 (C_6H_6) (Found: C, 30.35; H, 3.8; Br, 61.0. $C_{10}H_{15}Br_3O$ requires C, 30.72; H, 3.86; Br, 61.32%).

9-*Tribromomethyl*-8-*oxabicyclo*[5.2.1]*decane*: (21%), b.p. 80—83 °C/0.5 mmHg; t.l.c. R_F 0.72 (C_6H_6); $\nu_{max.}$ (film) 2 890, 2 800, 1 460, 1 435, 1 235, 1 190, 1 075, 910, and 670 cm^{-1}; δ 4.64—4.14 (2 H, complex m, 7-H + 9-H), 2.60—1.32 (*ca.* 13 H, br complex m, 1-H + ring CH_2).

Isoprene.—Reaction in CCl_4 in the presence of 2 mol% $AlCl_3$ for 30 min afforded, after esterification with acetic anhydride and then column chromatography, the ene adduct acetate, 1,1,1-*tribromo*-4-*methylenehex*-5-*en*-2-*yl acetate* [(46b) acetate], and the formal Diels–Alder adduct 6-*tribromomethyl*-4-*methyloxacyclohex*-3-*ene* (47b).

Compound [(46b) acetate]: (11.4%), b.p. 79—80 °C/0.02 mmHg; t.l.c. R_F 0.47 (C_6H_6); $\nu_{max.}$ (film) 3 070, 2 940, 1 750, 1 590, 1 445, 1 370, 1 210, 1 120, 1 050, 995, 910, 735, and 700 cm^{-1}; δ 6.72—5.32 (6 H, series of complex m, olefinic H + 2-H), 3.39 (1 H, br d, *J* 14 Hz, 3a-H), 2.70 (1 H, dd, separations 10 and 14 Hz, 3b-H), and 2.12 (3 H, s, $COCH_3$).

Compound (47b): (14.4%), b.p. 93—95 °C/0.5 mmHg; t.l.c. R_F 0.59 (C_6H_6) (Found: C, 24.35; H, 3.05. $C_7H_9Br_3O$ requires C, 24.10; H, 2.60%); $\nu_{max.}$ (film) 3 000, 2 900, 2 800, 1 665, 1 440, 1 375, 1 350, 1 160, 1 120, 735, 700, and 685 cm^{-1}; δ 5.47 (1 H, br s, 3-H), 4.45 (2 H, m, 2 × 2-H), 3.91 (1 H, dd,

separations 4 and 9 Hz, 6-H), 2.5—2.1 (2 H, br m, 2 × 5-H), and 1.81 (3 H, br s, CH_3).

Acknowledgements

We are indebted to the SERC for maintenance grants for J. P. B., S. J. P., and B. W., and for a grant for the purchase of the capillary column g.l.c. instrumentation. We are happy to acknowledge contributions to this study *via* undergraduate project work by Jean Morley, Jane Taylor, Barbara Tipple, Frederika Sarrou, Susan Christopher, Stephen Clements, Clare Moulds, David Maitland, Paul Gadd, and Stephen Frankham.

References

1 H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 556.
2 B. B. Snider, *Acc. Chem. Res.*, 1980, **13**, 426; B. B. Snider, D. J. Rodini, M. Karras, T. C. Kirk, E. A. Deutsch, R. Cordova, and R. T. Price, *Tetrahedron*, 1981, **37**, 3927; and references cited therein.
3 G. B. Gill and B. Wallace, *J. Chem. Soc., Chem. Commun.*, 1977, 380, 382; G. B. Gill, S. J. Parrott, and B. Wallace, *ibid.*, 1978, 655; G. B. Gill, K. Marrison, S. J. Parrott, and B. Wallace, *Tetrahedron Lett.*, 1979, 4867.
4 P. Yates and P. Eaton, *J. Am. Chem. Soc.*, 1960, **82**, 4436; E. F. Lutz and G. M. Bailey, *ibid.*, 1964, **86**, 3899; J. Sauer and J. Kredel, *Tetrahedron Lett.*, 1966, 731, 6359; T. Inukai and T. Kojima, *J. Org. Chem.*, 1966, **31**, 2032.
5 (*a*) J. P. Benner, G. B. Gill, S. J. Parrott, B. Wallace, and M. J. Begley, *J. Chem. Soc., Perkin Trans. 1*, 1984, following paper (*b*) *ibid.*, 331.
6 (*a*) J. Colonge and A. Perrot, *C.R. Hebd. Seances Acad. Sci.*, 1954, **239**, 541; (*b*) *Bull. Soc. Chim. Fr.*, 1957, 204, 658.
7 (*a*) H. Normant and J. Ficini, *Bull. Soc. Chim. Fr.*, 1956, 1441; (*b*) J. Farkaš, P. Kouřim, and F. Šorm, *Chem. Listy*, 1958, **52**, 688; *Coll. Czech. Chem. Commun.*, 1959, **24**, 2230.
8 E. I. Klimova, A. I. Abramov, N. D. Antonova, and Yu. A. Arbuzov, *Zh. Org. Khim.*, 1969, **5**, 1341; E. I. Klimova, N. D. Antonova, and Yu. A. Arbuzov, *ibid.*, p. 1348; E. I. Klimova, E. G. Treshchova, and Yu. A. Arbuzov, *ibid.*, 1970, **6**, 419; *Dokl. Akad. Nauk. SSSR*, 1968, **180**, 865.
9 M. J. Begley, J. P. Benner, and G. B. Gill, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1112.
10 (*a*) M. Vilkas, G. Dupont, and R. Doulou, *Bull. Soc. Chim. Fr.*, 1955, 799; (*b*) H. Fritz, C. D. Weis, and T. Winkler, *Helv. Chim. Acta*, 1975, **58**, 1345.
11 M. J. Begley, G. B. Gill, and B. Wallace, *J. Chem. Soc., Perkin Trans. 1*, 1978, **93**.
12 (*a*) A. E. Baydar, G. V. Boyd, R. L. Monteil, P. F. Lindley, and M. M. Mahmoud, *J. Chem. Soc., Chem. Commun.*, 1976, 650; (*b*) see however E. Kiehlmann, P.-W. Loo, B. C. Menon, and N. Gillivray, *Can. J. Chem.*, 1971, **49**, 2964.
13 A. I. Vogel, ' Practical Organic Chemistry,' 3rd edn., Longman (1956).
14 ' Organicum; Practical Handbook of Organic Chemistry,' English translation by B. J. Hazzard, Pergamon Press, 1973.
15 E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1950, 2017.
16 Y. Sakurada, M. L. Huggins, and W. R. Anderson, Jr., *J. Phys. Chem.*, 1964, **68**, 1934.
17 P. Mastagli and F. de Champs, *C.R. Hebd. Seances Acad. Sci.*, 1970, **270**, 1247.
18 ' Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 4th edn., 1965.
19 R. Bowman and W. R. N. Williamson, *J. Chem. Soc., C*, 1970, 101.

Received 27*th January* 1983; *Paper* 3/117