

Gold(III) as an Electrophilic Oxidant of Alkenes

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The products of oxidation of a variety of olefins by tetrachloroauric acid in methanol are reported. They are satisfactorily accounted for by a scheme in which gold(III) acts as an electrophile to give an organometallic adduct; this breaks down by heterolysis of the C–Au bond, accompanied by competition between rearrangement of a neighbouring substituent and uptake of a nucleophile. In all cases a close similarity was observed with the products obtained from oxidations by thallium(III) and lead(IV); where divergences occur they can be accounted for in terms of either the different ligands about the metal atom or the different leaving-group abilities of the metal substituents.

IN recent papers^{1–3} we compared the organic products formed in the oxidation of typical alkenes by mercury(II), thallium(III), and lead(IV) salts, the primary emphasis being on the mechanistic aspects of the reaction. In most cases a mixture of products is obtained but, under certain conditions, the reaction can be made synthetically useful.^{3–5} Usually the initial step is electrophilic attack on the double bond by the oxidant, which is followed by heterolysis of the carbon–metal bond in the resultant labile organometallic species. We sought other metal oxidising agents with comparable properties, in the hope that they might prove mechanistically and synthetically interesting. The metal must be a two-electron oxidant, so that electrophilic metallation will occur. Unfortunately such elements are rare. Apart from the above three, the only other obvious candidates are platinum, palladium, gold, and tin. The first two, especially palladium(II), have been extensively investigated, but our ability to predict and control the products of their reactions with most alkenes is still limited;⁶ certainly the characteristics normally associated with electrophilic addition are not particularly evident with these two metals. In this paper we consider the usefulness of gold as a two-electron oxidant of alkenes.

The first olefin–gold(III) complex, that with cyclo-octa-1,4-diene, was identified as recently as 1964.⁷ Such complexes are even less stable than those of gold(I), which themselves are difficult enough to isolate, decomposing to give the free alkene at temperatures little above ambient.⁸ Indeed there appear to be no authenticated examples of complexes of gold(III) with simple alkenes, though mixed gold(I)–gold(III) complexes have been identified.⁹

The few studies to date of the reactions of gold oxidants with alkenes have been primarily directed at organometallic aspects of the process, but two reports have appeared of the organic products. The first was a patent covering the production of aldehydes and ketones by reaction with tetrachloroauric acid.¹⁰ The second

(more detailed) listed the products from treatment of several alkenes with tetrachloroauric acid in water and with gold(III) chloride in non-nucleophilic solvents.⁹ The compounds obtained in both cases are consistent with the occurrence of electrophilic attack on the double bond by gold(III) followed by heterolysis of the carbon–gold bond after the manner of oxidations with mercury(II), thallium(III), and lead(IV). However, alternative routes to the products are possible and our study was designed to test whether gold(III) does in fact behave as an electrophile towards alkenes.

In order to make comparison with mercury, thallium, and lead easier we would have liked to use gold(III) acetate, but this appears to be unknown. Acetatoaurate salts have been reported but are not soluble in organic solvents.¹¹ Only the halides and the corresponding acids of formula HAuHal₄ are commonly available. Tetrachloroauric acid is hygroscopic¹² and is very soluble in water, acetic acid, alcohols, and even ether. By comparison, the covalent trichloride offers little advantage as it too is hygroscopic and in the presence of moisture tends to form the tetrachloroaurate anion.¹³ We therefore chose tetrachloroauric acid as the oxidant and, in order to be able to compare the results with those of earlier studies, methanol as solvent.

RESULTS AND DISCUSSION

The first alkene oxidised was oct-1-ene. Four products, (1)–(4), were obtained after refluxing with tetrachloroauric acid in methanol for 24 h. Their yields are set out in Table I together with the products of oxidation with thallium(III) and lead(IV) under similar conditions. Allowing for the difference in ligands about the metal it can be seen that gold(III) gives similar products to the other two metal oxidants, suggesting a common mode of reaction, *viz.* electrophilic addition followed by heterolysis of the carbon–metal bond.^{1–3} The one exception is the chloro-ketone (2).

⁶ For a wide-ranging review of this field see P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971.

⁷ A. J. Chalk, *J. Amer. Chem. Soc.*, 1964, **86**, 4733.

⁸ R. Hüttel and H. Reinheimer, *Chem. Ber.*, 1966, **99**, 2778.

⁹ R. Hüttel, H. Reinheimer, and K. Nowak, *Tetrahedron Letters*, 1967, 1019; *Chem. Ber.*, 1968, **101**, 3761.

¹⁰ F. Dean, B.P. 879,197 (*Chem. Abs.*, 1962, **56**, 12,744e).

¹¹ 'Nouveau Traité de Chimie minérale,' ed. P. Pascal, Masson, Paris, 1957, vol. 3, p. 798.

¹² Ref. 11, p. 758.

¹³ N. Bjerrum, *Bull. Soc. chim. belges*, 1948, **57**, 432.

¹ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1974, 1929.

² A. Lethbridge, R. O. C. Norman, C. B. Thomas, and W. J. E. Parr, *J.C.S. Perkin I*, 1975, 231.

³ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1975, 2465.

⁴ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1973, 35.

⁵ A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1973, **95**, 3635.

No analogues of this compound were detected in oxidations with the other two metals. The difference probably arises because, under the anhydrous conditions used previously, 2,2-dimethoxyoctane, the precursor of (1), is largely stable, hydrolysis to the ketone only occurring during work-up. With tetrachloroauric acid,

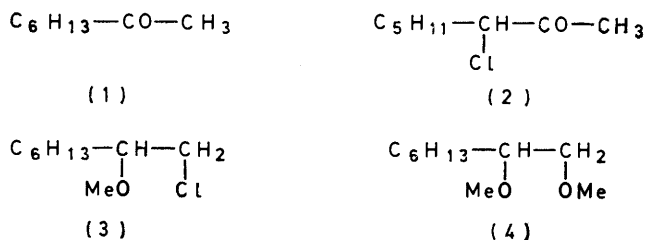
TABLE I

Products from the oxidation of oct-1-ene by metal electrophiles in methanol

Oxidant	Products (%)				Methoxyacetate adducts
	(1)	(2)	(3)	(4)	
HAuCl ₄	36	17	5.0	12	
Pb(OAc) ₄ ^a	28		5.0 ^b	52	13
Tl(OAc) ₃ ^a	5.6			10	77

^a From ref. 1. ^b From chloride impurity.

not only is water present from the oxidant, but so is a strong acid, so that octan-2-one will be generated *in situ* and its enol form will react readily with the oxidant to yield (2). A control experiment confirmed that (1) is converted into (2) under the reaction conditions. The formation of 3-chloro-octan-2-one requires two equivalents of oxidant so that the total conversion of oct-1-ene by gold(III) is high.



It might be argued that the electrophile giving rise to the products is not gold(III), but chlorine produced by thermal decomposition of tetrachloroauric acid.¹⁴ Two observations suggest that this is not the case. First, reaction of chlorine with a terminal alkene in methanol would be expected to lead not only to 1-chloro-2-methoxyalkane but also to 1,2-dichloroalkane; although the reaction of chlorine with oct-1-ene in alcoholic solvents has not been reported, this is certainly true of propene.¹⁵ However, no dichloride was detected in our system. Secondly, there is no obvious way in which compounds (1), (2), and (4) could arise by attack of chlorine on oct-1-ene unless one of the initial products were to react further. It seems unlikely, even with a Lewis acid present, that this would happen so completely. Copper(II) chloride, under much more severe conditions,¹⁶ gave with oct-1-ene in methanol, both (3) and 1,2-dichloro-octane with, apparently, no other products. In

¹⁴ Ref. 11, p. 748.

¹⁵ W. Vogt and H. Richtzenhain, W.Ger.P. 1,250,805 (*Chem. Abs.*, 1968, **68**, 95, 329).

¹⁶ G. Bressan and R. Broggi, *Chimica e Industria*, 1967, **49**, 1074.

¹⁷ W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 61.

¹⁸ W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, 1957, **79**, 3469.

addition, as we note later, closely related compounds were unchanged after subjection to the reaction conditions.

It is not clear whether a π -olefin complex mediates. As noted above, such complexes have never been identified though they have been proposed as intermediates in gold(III) oxidations (*e.g.* ref. 9). However, this is of minor importance, for a similar situation applies to oxidation by mercury(II),¹⁷ which, whilst showing all the characteristics of an electrophilic addition,¹⁻³ nevertheless is considered to involve initial formation of an uncharacterisable π -complex. Presumably such a species represents a small well on the energy profile from reactants to the transition state which precedes the mercurio-cation intermediate.²

On the basis therefore that gold(III) is the electrophile, a mechanism for the formation of the products is that shown in Scheme 1 where, for simplicity, positively charged intermediates are assumed to be free carbocations. Comparison of the ratio of 1,2-adducts to the products resulting from hydride shift in Table I suggests that carbocation character in the heterolysis of a carbon-metal bond increases in the order Tl < Pb < Au,³ *i.e.* that AuCl₂ is a better leaving group than either Tl(OAc)₂ or Pb(OAc)₃.

Five other monosubstituted alkenes were oxidised with tetrachloroauric acid. 3-Phenylpropene, 4-phenylbut-1-ene, and 5-phenylpent-1-ene all gave, as the major product, the corresponding methyl ketone (yields 35, 43, and 54%, respectively) with lesser amounts of 1,2-dimethoxy- and 1-chloro-2-methoxy-adducts and of chloro-ketones. In the case of 4-phenylbut-1-ene the two 1,2-adducts were obtained in yields of 9 and 14%, respectively, and it was demonstrated that the dichloride and the methoxy-chloride were both unchanged after treatment with the oxidant in refluxing methanol.

Oxidation of 3,3-dimethylbut-1-ene gave 27% of 3,3-dimethylbutan-2-one. The g.l.c.-mass spectra of the other products were not consistent with compounds derived from methyl migration following initial uptake of an electrophile but were in accord with simple 1,2-adducts. Rearrangement is not a prerequisite of electrophilic addition to this alkene; for instance, neither bromine¹⁸ nor mercury(II) acetate¹⁹ leads to rearrangement products yet both are undoubtedly electrophilic in nature. Methyl migration is apparently confined to those systems in which there is little stabilisation of the carbocation centre by the new β -substituent. On that basis we presume there must be significant interaction between the AuCl₂ group and the positive centre in our system.

3,3,3-Triphenylpropene is much more prone to skeletal rearrangement during addition reactions; for instance, with bromine²⁰ and with lead(IV) acetate²¹ the only

¹⁹ H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, 1969, **91**, 5646; H. C. Brown and J. T. Kurek, *ibid.*, p. 5647; H. C. Brown and P. J. Geoghegan, *J. Org. Chem.*, 1970, **35**, 1844.

²⁰ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 598; A. Hassner and J. S. Teeter, *J. Org. Chem.*, 1971, **36**, 2176.

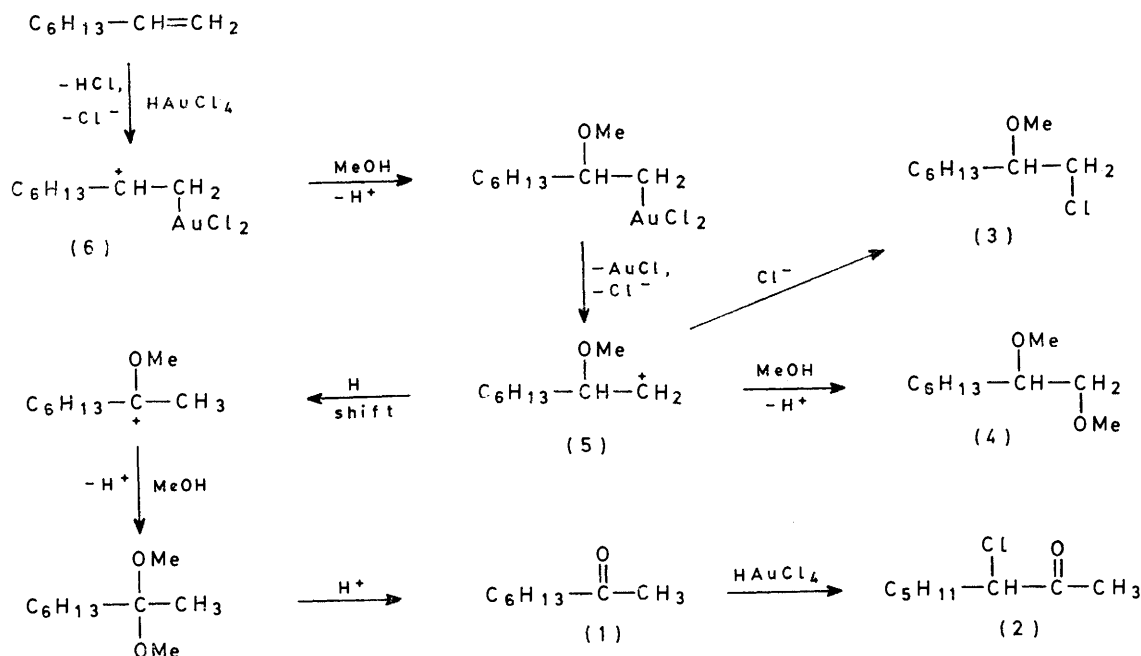
²¹ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 604.

products arising by ionic routes, albeit sluggishly, are ones in which a phenyl group has migrated. Unfortunately, however, gold(III) did not react, presumably as a result of the alkene's reluctance to react with bulky electrophiles.

The reaction of styrene with metal oxidants is well documented. Usually rearrangement predominates,

only significant products, benzyl methyl ketone and 2-methoxy-2-phenylpropane.

Of the 1,2-adducts there was no evidence for the dimethoxy-compound and, in contrast to the behaviour of aliphatic olefins, dichloride was formed. Acetophenone has not been reported to be formed with other metal oxidants and its presence may indicate the greater



leading to derivatives of phenylacetaldehyde.^{5,22,23} Oxidation of styrene gave six products, (7)—(12), the yields of which are in Table 2. The first of these is the

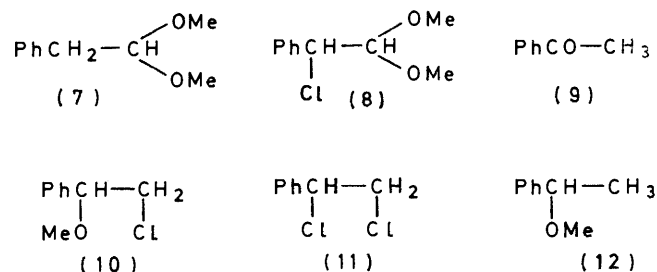
ease of heterolysis of carbon-gold bonds; there would then be less need for neighbouring group participation and hence a lower selectivity in rearrangement, allowing hydride shift to compete with phenyl shift. The

TABLE 2
Products from the oxidation of styrene by metal electrophiles in methanol

Oxidant	Products (%)		
	Phenyl-acetaldehyde derivatives	1,2-Adducts	Others
HAuCl ₄	57 ^a	8 ^b	30 ^c
Pb(OAc) ₄ ^d	70 ^e	f	
Tl(OAc) ₃ ^d	69 ^g	f	

^a 1,1-Dimethoxy-2-phenylethane (47%) and 2-chloro-1,1-dimethoxy-2-phenylethane (10%). ^b 1-Chloro-2-methoxy-2-phenylethane (2%) and 1,2-dichloro-1-phenylethane (6%). ^c 1-Methoxy-1-phenylethane (27%) and acetophenone (3%). ^d Ref. 22. ^e 1,1-Dimethoxy-2-phenylethane and 1-acetoxy-1-methoxy-2-phenylethane. ^f Products identified after hydrolysis; yields not quoted. ^g 1,1-Dimethoxy-2-phenylethane.

product we should expect from the mechanism shown in Scheme 2a. An alternative mode of formation, from an anti-Markownikov adduct (Scheme 2b), was discounted when it was found that 2-phenylpropene gave, as the



formation of compound (12) is unexpected: no such products were detected with simple alkenes. Certainly there is acid present to catalyse the addition of methanol and it may be that attack by a proton is more sensitive to electronic factors than is attack by gold(III). A similar situation applies to lead(IV) oxidations in trifluoroacetic acid; proton uptake on the double bond competes much more effectively with lead(IV) uptake in the case of arylalkenes⁴ than in the case of oct-1-ene.²

With thallium(III) (in methanol)^{5,24} and lead(IV) (in
²⁴ L. Nadon, M. Tardat, M. Zador, and S. Fliszar, *Canad. J. Chem.*, 1973, **51**, 2366.

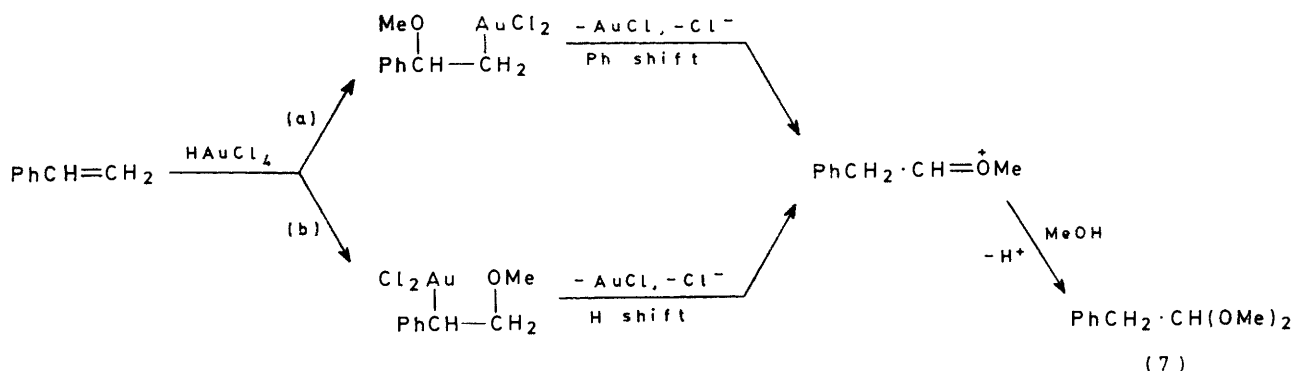
²² H.-J. Kabbe, *Annalen*, 1962, **656**, 204.

²³ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 771.

acetic acid²⁵ and in trifluoroacetic acid⁴), 1,1-diphenylethene yields deoxybenzoin. However, this was not the case with tetrachloroauric acid, the only products being 1-chloro-2-methoxy-2,2-diphenylethane and 1-chloro-2,2-diphenylethene, both of which are the expected products of reaction of chlorine with the alkene in

electrophilic addition is *trans*, the heterolysis of the carbon-metal bond must occur with inversion of configuration about that carbon atom; *i.e.* in an S_N2 -like process.

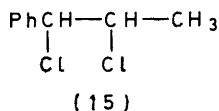
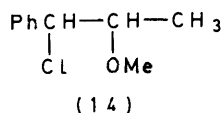
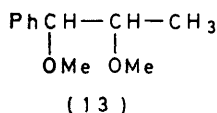
Dichloride formation appears to be confined to aryl-substituted olefins. A possible explanation, if chloride



SCHEME 2

methanol. It is possible that the steric factors, which we have suggested are of considerable importance in governing the reactivity of a particular alkene, now become over-riding. Unable to attack the double bond, the tetrachloroauric acid slowly disproportionates and the resultant chlorine now acts as the electrophile.

As a check on the stereochemistry of addition we next investigated the oxidation of *trans*-1-phenylpropene. In line with its reduced capacity, in comparison with styrene, to undergo rearrangement on oxidation with lead(IV),^{4,26} treatment with tetrachloroauric acid led to no derivatives of 2-phenylpropanal. Six compounds were identified, namely (13) (4.5%; *erythro*: *threo* 62:38), (14) (49%; 61:39), and (15) (14%; 10:90).



The stereoselectivity of formation of (15) is not only the reverse of, but is much greater than, that reported for the addition of chlorine to *trans*-1-phenylpropene,²⁷ implying that disproportionation of tetrachloroauric acid to chlorine is not the source of the dichlorides. These compounds more probably arise by decomposition of an organo-gold species in which chloride has been taken up on the benzylic carbon atom. Assuming that initial

ion is more strongly nucleophilic than methanol, is that in these cases the positively charged species analogous to (6) is more stable as a result of delocalisation of the charge over the aromatic ring, and therefore more selective towards nucleophiles. Such a suggestion is also compatible with the formation of (14), methanol being the nucleophile displacing the gold(III) group. (All other chloro-methoxy-adducts have resulted from chloride uptake on the carbon atom to which the gold electrophile was attached.) However, the different stereoselectivity in comparison with (15) suggests there is likely to be a competitive route to (14). This is probably the one involving migration of the methoxy-substituent from C-1 to C-2 during displacement of a metal leaving group,¹ a process which would be expected to result in the *erythro*-isomer rather than the *threo*. In support of this suggestion, in the reaction of 1-phenylpropene with chlorine in methanol, stereoselectivity was greater for the mixed adduct than for the dichloride.²⁷

With an aliphatic internal alkene, *trans*-oct-4-ene, the similarity of oxidation by gold(III) to oxidations by thallium(III) and by lead(IV) is again apparent (Table 3). Like the other two oxidants, gold(III) reacted sluggishly and left a considerable amount of unchanged alkene. Similarly, allylic ethers were formed, though in relatively smaller amounts, consistent with the suggestion that, at least for lead(IV), these originate primarily by a radical abstraction process for which there is no evidence in the case of gold(III).² Unfortunately it proved impossible to separate the diastereoisomers of 4,5-dimethoxyoctane by gas chromatography and so to investigate the stereochemical aspect of the reaction. Broadly similar results were obtained with cyclohexene, with the notable exception, for which we have no explanation, of the absence of any cyclopentanecarb-

²⁵ C. B. Thomas, D.Phil. Thesis, York, 1967.

²⁶ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1968, 994.

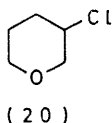
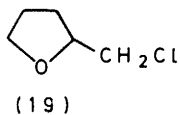
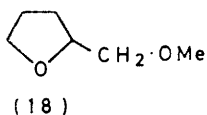
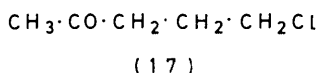
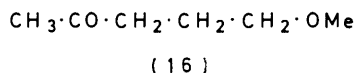
²⁷ R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 5172.

TABLE 3
Products from the oxidation of *trans*-oct-4-ene by metal electrophiles in methanol

Oxidant	Products (%)			
	$C_3H_7COC_4H_9$	Allylic ethers ^a	$C_3H_7\cdot CH(OMe)\cdot CH(OMe)\cdot C_3H_7$	$C_3H_7\cdot CHCl\cdot CH(OMe)\cdot C_3H_7$
$HAuCl_4$	13	8	20	5
$Pb(OAc)_4^b$	3	6	5	
$Tl(OAc)_3^b$	4	8	3.5	

^a Mixture of 3-methoxyoct-4-ene and 5-methoxyoct-3-ene. ^b Ref. 2.

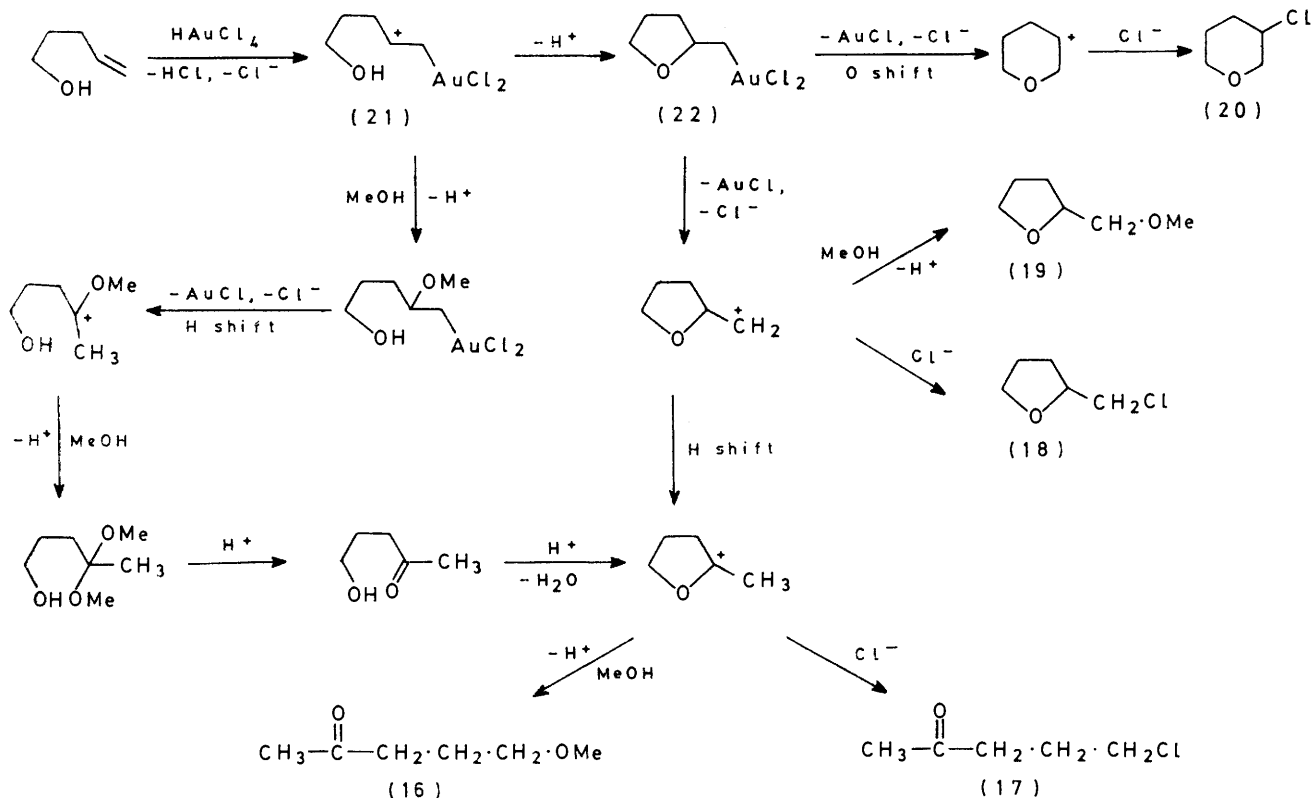
aldehyde derivatives (cf. refs. 5 and 22). Once again gas chromatographic resolution of the isomeric 1,2-di-



methoxy-adducts proved impossible but we did carry out a reaction, albeit a sluggish one, in acetic acid from which,

after acetylation, the 1,2-diacetates were separable. The *cis*:*trans* ratio of the adducts was 92:8, consistent with initial *trans*-addition of the electrophile to the double bond followed by formation of the hydroxy-acetates *via* an acetoxonium ion intermediate.

As final proof of the mediation of carbocations in oxidations by gold(III) we looked for neighbouring-group participation by oxidising pent-4-en-1-ol. Five products, (16)–(20), three of them cyclic, were obtained. Compounds (18) (11%) and (19) (4.9%) can be accounted for most easily by nucleophilic attack of the hydroxy-group on the initial carbocation (21) (Scheme 3). Similarly (20) (2.2%) could arise from the organo-gold adduct (22) by oxygen migration,^{1,3} though the absence of 3-methoxypyran is difficult to explain without invoking ion-pair intervention.¹ We demonstrated that the two acyclic products (12 and 13%, respectively) could be formed under the reaction conditions from 5-hydroxypentan-2-one, presumably *via* a cyclic oxonium ion, and they may therefore represent a pathway in which solvent attack competes successfully with the neighbouring group for the ion (21). Alternatively they may result



SCHEME 3

from hydride shift in the decomposition of the dichloroauriomethyltetrahydrofuran derivative (22).

EXPERIMENTAL

The general experimental procedures and many of the substrates and products have been described previously.^{1,2,4,21,26,28} 3-Phenylpropene, 3,3-dimethylbut-1-ene, 5-chloropentan-2-one (Fluka), pent-4-en-1-ol, 4-phenylbutan-2-one, and 3,3-dimethylbutan-2-one (Koch-Light) were commercially available. Other materials were made as follows.

3-Chloro-octan-2-one. Sulphuryl chloride (6.7 g) was added dropwise to octan-2-one (6.4 g) at 0 °C. After stirring for 5 h, the more volatile components were removed by rotary evaporator and the residue distilled to give a fraction, b.p. 85–90° at 12 mmHg, which was subjected to preparative g.l.c. to give 3-chloro-octan-2-one (lit.,²⁹ b.p. 70–75° at 10 mmHg); τ 5.84 (1 H, t, *J* 7 Hz, CH), 7.72 (3 H, s, CH₃), and 7.9–9.4 (11 H, aliphatic envelope).

1-Chloro-2-methoxyoctane. Chlorine was passed into a solution of oct-1-ene (11 g) in methanol (30 ml) at 0 °C until an excess was present. Removal of the solvent followed by distillation gave a fraction, b.p. 92–93° at 12 mmHg, which was further purified by preparative g.l.c. to yield 1-chloro-2-methoxyoctane; τ 6.47 (2 H, t, *J* 5 Hz, CH₂·OMe), 6.6–6.9 (1 H, m, CH), 6.61 (3 H, s, OCH₃), and 8.0–9.3 (13 H, aliphatic envelope).

1,2-Dimethoxy-4-phenylbutane. Lead(IV) acetate (19.6 g) was added to a stirred solution of 4-phenylbut-1-ene (5.3 g) in methanol (30 ml). The solution was stirred for 1 h at 60 °C and poured into water, and the ethereal extract was washed with sodium hydrogen carbonate solution and water and dried (MgSO₄). Removal of the solvent followed by preparative g.l.c. gave 1,2-dimethoxy-4-phenylbutane; τ 2.85 (5 H, s, ArH), 6.64 and 6.72 (2 s, 2 OMe) and 6.55–6.95 (m, CH·CH₂) (total 9 H), 7.34br (2 H, t, *J* 7.5 Hz, CH₂Ar), and 8.0–8.6 (2 H, m, CH₂·CH₂Ar) (Found: C, 74.8; H, 9.3. C₁₂H₁₈O₂ requires C, 74.2; H, 9.3%).

1-Chloro-2-methoxy-4-phenylbutane was isolated by preparative g.l.c. from a large-scale oxidation of 4-phenylbut-1-ene with tetrachloroauric acid. It had τ 2.83 (5 H, s, ArH), 6.61 (s, OMe) and 6.45–6.90 (m, CH·CH₂Cl) (total 6 H), 7.31br (2 H, t, *J* 7.5 Hz, CH₂Ar), and 7.9–8.3 (2 H, m, CH₂·CH₂Ar) (Found: C, 66.3; H, 7.5. C₁₁H₁₅ClO requires C, 66.5; H, 7.6%).

1,2-Dichloro-4-phenylbutane. Chlorine was passed into a solution of 4-phenylbut-1-ene (6.4 g) in carbon tetrachloride (20 ml) at 0 °C until an excess was present. Removal of the solvent and distillation afforded 1,2-dichloro-4-phenylbutane, b.p. 138–139° at 13 mmHg; τ 2.82 (5 H, s, ArH), 6.0–6.6 (3 H, m, CHCl·CH₂Cl), and 7.0–8.4 (4 H, m, CH₂CH₂Ph).

1,1-Dimethoxy-2-phenylethane. Toluene-*p*-sulphonic acid (2 g) and freshly distilled phenylacetaldehyde (20 g) were refluxed in methanol (100 ml) for 24 h. The solution was cooled, poured into water, and extracted with ether, and the extracts were washed with sodium hydrogen carbonate solution and water, and dried (MgSO₄). Removal of the solvent followed by distillation gave 1,1-dimethoxy-1-

phenylethane, b.p. 98° at 12 mmHg (lit.,³⁰ 95–99° at 10 mmHg); τ 2.71 (5 H, s, ArH), 5.45 (1 H, t, *J* 6 Hz, CH), 6.68 (6 H, s, OCH₃), and 7.09 (2 H, d, *J* 6 Hz, CH₂).

2-Chloro-1,1-dimethoxy-2-phenylethane. Sulphuryl chloride (6.0 g) was added dropwise to a solution of phenylethanal (5.0 g) in dry dichloromethane (20 ml) at 0 °C. After stirring for 1 h at 20 °C, the solvent was removed and the residue distilled to give 2-chloro-2-phenylethanal, b.p. 98° at 12 mmHg (lit.,³¹ 98–100° at 13 mmHg). The aldehyde (2.0 g) was dissolved in methanol (50 ml) containing toluene-*p*-sulphonic acid (0.5 g) and the solution was refluxed for 24 h, cooled, poured into water, and extracted with ether; the extracts were washed with sodium hydrogen carbonate solution and water, and dried (MgSO₄). Removal of the solvent left an oil from which 2-chloro-1,1-dimethoxy-2-phenylethane was isolated by preparative g.l.c.; τ 2.65 (5 H, s, ArH), 5.19 (1 H, d, *J* 6 Hz, CH), 5.34 (1 H, d, *J* 6 Hz, CH), 6.58 (3 H, s, OCH₃), and 6.79 (3 H, s, OCH₃) (Found: C, 60.2; H, 6.3. C₁₀H₁₃ClO₂ requires C, 59.9; H, 6.5%).

2-Chloro-1-methoxy-1-phenylethane was prepared as for 1-chloro-2-methoxyoctane. Preparative g.l.c. of the fraction of b.p. 92–93° at 13 mmHg gave 2-chloro-1-methoxy-1-phenylethane (lit.,³² b.p., 101–105° at 15 mmHg); τ 2.60 (5 H, s, ArH), 5.61 (1 H, t, *J* 6 Hz, CH), 6.36 (2 H, d, *J* 6 Hz, CH₂), and 6.70 (3 H, s, OCH₃).

1,2-Dichloro-1-phenylethane was prepared as for 1,2-dichloro-4-phenylbutane and had b.p. 110° at 12 mmHg (lit.,³³ 114.5–115.5° at 15 mmHg); τ 2.64 (5 H, s, ArH), 5.07 (1 H, dd, *J* 9 and 6 Hz, CH), and 6.13 (2 H, dd, *J* 9 and 6 Hz, CH₂).

1-Methoxy-1-phenylethane. A solution of styrene (30 ml) in methanol (100 ml) containing sulphuric acid (3 ml) and a few crystals of hydroquinone was refluxed under nitrogen for 24 h, poured into water, and extracted with ether. The extracts were washed with sodium hydrogen carbonate solution and water, and dried (MgSO₄). Removal of the solvent and distillation of the residue gave 1-methoxy-1-phenylethane, b.p. 56° at 12 mmHg (lit.,³⁴ 71–76° at 32 mmHg); τ 2.64 (5 H, s, ArH), 5.70 (1 H, q, *J* 6 Hz, CH), 6.77 (3 H, s, OCH₃), and 8.56 (3 H, d, *J* 6 Hz, CH₃).

1-Chloro-2,2-diphenylethene. Chlorine was passed into a solution of 1,1-diphenylethene (5 g) in methanol (20 ml) until a yellow colour persisted. The solvent was removed and the residue distilled to yield 1-chloro-2,2-diphenylethene, b.p. 300–302° (lit.,³⁵ 130–137° at 1 mmHg); τ 2.60 and 2.72 (10 H, 2s, ArH), and 3.39 (1 H, s, CH=).

2-Chloro-1-methoxy-1,1-diphenylethane. 1,1-Diphenylethylene (1 g) and tetrachloroauric acid (2 g) in methanol (20 ml) were refluxed for 2 days; the mixture was then cooled, poured into water, and extracted with ether. The extracts were washed with sodium hydrogen carbonate solution and dried (MgSO₄). Removal of the solvent followed by preparative g.l.c. gave 2-chloro-1-methoxy-1,1-diphenylethane, τ 2.70 (10 H, s, ArH), 5.75 (2 H, s, CH₂), and 6.90 (3 H, s, OCH₃) [Found: *m/e* 214.0543 and 197.0966. C₁₄H₁₁³⁵Cl (M – OMe) requires 214.0549. C₁₄H₁₃O (M – CH₂Cl) requires 197.0966].

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1,2-Dimethoxy-1-phenylpropane. A solution of lead(IV) acetate (19.6 g) and *trans*-1-phenylpropane (4.73 g) in methanol (60 ml) was stirred at 60 °C for 3 h, cooled, poured into water, and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate and water and dried (MgSO₄). Removal of the solvent followed by preparative g.l.c. afforded 1,2-dimethoxy-1-phenylpropane as a *threo-erythro*-mixture, τ 2.71 (5 H, s, ArH), 5.85—6.1 (1 H, m, CHPh), 6.68 and 6.85 (2s, OCH₃) and 6.5—7.0 (m, CH·CH₃) (total 7 H), 8.92 (3 H, d, *J* 6 Hz, *erythro* CH₃³⁶), and 9.25 (3 H, d, *J* 6 Hz, *threo* CH₃³⁶) (Found: C, 73.5; H, 8.9. C₁₁H₁₆O₂ requires C, 73.3; H, 9.0%).

2-Chloro-1-methoxy-1-phenylpropane, prepared in the same way as 1-chloro-2-methoxyoctane, was obtained by preparative g.l.c. of the fraction of b.p. 108—110° at 14 mmHg. The ¹H n.m.r. spectrum was as previously reported.²⁷

1-Chloro-2-methoxy-1-phenylpropane was isolated from a large scale oxidation by tetrachloroauric acid of *trans*-1-phenylpropene, by preparative g.l.c. The two diastereoisomers were not resolvable under these conditions; τ 2.67 (5 H, s, ArH), 5.31 (1 H, d, *J* 7 Hz, CHCl·CHOMe), 6.72 (3 H, s, OCH₃), 6.5—7.0 (1 H, m, CHOMe), 8.86 (3 H, d, *J* 6 Hz, *erythro*-CH₃³⁶), and 9.04 (3 H, d, *J* 6 Hz, *threo*-CH₃³⁶) [Found: *m/e* 184.0660, 125.0162, and 59.0498. C₁₀H₁₃³⁵ClO (*M*⁺) requires 184.0665. C₇H₆³⁵Cl (*M* - CH₃CHOMe) requires 125.0158. C₃H₇O (CH₃CH=O⁺Me) requires 59.0497].

1,2-Dichloro-1-phenylpropane (*erythro-threo*-mixture) was prepared in the same way as 1,2-dichloro-4-phenylbutane and had b.p. 118—120° at 14 mmHg (lit.³⁷ 110—113° at 11 mmHg); ¹H n.m.r. spectrum as previously reported.²⁷

5-Chloro-4-methoxyoctane was prepared as for 1-chloro-2-methoxyoctane from *trans*-oct-4-ene and was isolated by preparative g.l.c.; τ 5.8—6.2 (1 H, m, CHCl), 6.6—6.9 (1 H, m, CHOMe), 6.68 (3 H, s, OCH₃), and 8.1—9.3 (14 H, aliphatic envelope) (Found: C, 59.9; H, 10.5. C₉H₁₉ClO requires C, 60.5; H, 10.6%).

trans-1,2-Dimethoxycyclohexane. *trans*-Cyclohexane-1,2-diol (3.5 g) was dissolved in iodomethane (20 g) and silver(I) oxide (16 g) added. The resultant paste was stirred at 100 °C for 6 h, then cooled; the solids were filtered off, and the filtrate was poured into water and extracted with ether. The extracts were dried (MgSO₄) and evaporated and the residue was subjected to preparative g.l.c. to give *trans*-

1,2-dimethoxycyclohexane; τ 6.72 (6 H, s, OCH₃), 6.9—7.2 (2 H, m, CH), and 8.0—9.0 (8 H, aliphatic envelope).

5-Methoxypentan-2-one. 5-Chloropentan-2-one (6 g) and silver nitrate (17 g) in methanol (30 ml) were refluxed for 4 h; the solution was cooled, filtered, and evaporated. The residue was purified by preparative g.l.c. to give 5-methoxypentan-2-one, τ 6.70 (2 H, *J* 6 Hz, CH₂·OMe), 6.82 (3 H, s, OCH₃), 7.61 (2 H, t, *J* 7 Hz, CO·CH₂), 7.95 (3 H, s, CH₃·CO), and 7.9—8.6 (4 H, m, CH₂·CH₂).

2-Methoxymethyltetrahydrofuran. Sodium (0.35 g) was dissolved in tetrahydrofurfuryl alcohol (2.5 g). Iodomethane (2.1 g) was added and the mixture was refluxed for 2 h. After cooling, the filtrate was distilled to give 2-methoxymethyltetrahydrofuran, b.p. 41° at 14 mmHg (lit.³⁸ 141—144°); τ 5.8—6.4 (5 H, m, MeOCH₂·CH·O·CH₂), 6.60 (3 H, s, OCH₃), and 7.8—8.4 (4 H, m, CH₂·CH₂).

3-Chlorotetrahydropyran. A solution of 2,3-dihydropyran (16.8 g) in ether (40 ml) was cooled to 0 °C and chlorine passed in until an excess was present. The solvent was removed and the residual oil distilled to give 2,3-dichlorotetrahydropyran (11 g, 35.1%), b.p. 75—76° at 12 mmHg (lit.³⁹ 86—90° at 20 mmHg). The dichloride (8 g) in ether (20 ml) was stirred for ½ h at 20 °C with lithium aluminium hydride (0.5 g). The excess of reagent was destroyed with moist ether and dilute sulphuric acid, and the ether layer was separated and dried (MgSO₄). Removal of the solvent followed by distillation gave 3-chlorotetrahydropyran, b.p. 46—47° at 12 mmHg (lit.³⁹ 52—54° at 13 mmHg); τ 5.8—6.9 (5 H, m, CH·CH₂·O·CH₂) and 7.4—8.6 (4 H, m, CH₂·CH₂).

Oxidation.—The general oxidation procedure was as follows. The alkene (0.0015 mol) was added to a solution of tetrachloroauric acid (0.0005 mol) in methanol (10 ml) and the mixture was refluxed for the desired time. Gold metal normally precipitated during this period and, after cooling, was filtered off. The filtrate was poured into water and the ethereal extract was washed with sodium hydrogen carbonate solution and water, and dried (MgSO₄). The bulk of the solvent was removed and the residue subjected to g.l.c. analysis after addition of a standard. Products were identified by comparison of their retention times and mass spectra with those of authentic samples.

We thank the S.R.C. for a Studentship (to W. J. E. P.)

[5/2015 Received, 15th October, 1975]

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