

The Reactions of Alkynes, Cyclopropanes, and Benzene Derivatives with Gold(III)

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The reactions of gold(III) compounds with alkynes, arenes, and cyclopropanes have been studied. With the first two, the products can be accounted for in terms of electrophilic attack by the metal on the unsaturated centre. The reaction with alkynes bears a close resemblance to the mercury(II)-catalysed hydration but leads to higher conversions. Aromatic compounds react to give chloroarenes, the isomer distribution being consistent with initial metallation of the ring followed by replacement of the dichlorogold group by a chlorine atom. However, isolation of the intermediate arylgold compounds did not prove possible. Cyclopropanes were not oxidised to the expected 1,3-adducts; instead 1,2-adducts resulting from initial gold(III)-catalysed isomerisation to an alkene were obtained.

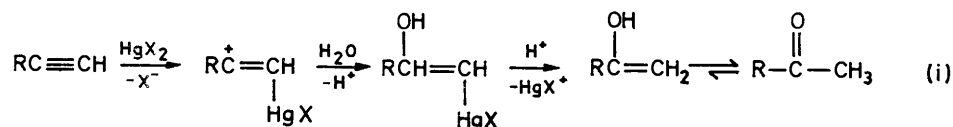
In a recent paper¹ we provided evidence that gold(III) reacts with alkenes in an electrophilic manner to give products of similar type to those obtained in mercury(II), thallium(III), and lead(IV) oxidations. We have now extended the study to other unsaturated species.

RESULTS AND DISCUSSION

Alkynes.—The mercury(II)-catalysed hydration of ethyne has long been known² as an industrially important route to ethanal. With monosubstituted alkynes, methyl ketones result.³ Although reports in the literature are fragmentary,⁴ the general consensus of opinion with regard to the mechanism favours electrophilic attack on the alkyne by mercury(II) to give an organomercury compound, from which the metal is displaced by a proton [reaction (i)]. Whether a mercury

products being highly dependent upon the structure of the organic substrate.⁷ Lead(IV) acetate, on the other hand, apparently gives simple products of electrophilic attack,⁸ though with phenylethyne only products from homolytic reaction are obtained.⁹

A number of aliphatic and aromatic alkynes were treated with tetrachloroauric acid in methanol under reflux for 24 h. Invariably the major products were the expected ketones, but small amounts (<5%) of what appeared, from g.l.c.–mass spectrometry, to be vinyl chlorides and methyl vinyl ethers were obtained. The yields, based on gold(III), are in Table 1. The alkyne was present in 3-fold excess, except in the case of phenylethyne where a 15-fold excess was employed, in order to check whether the conversion was catalytic with respect to gold(III). As can be seen, this was so in many



π -complex is initially formed⁵ has never been established, though the formally somewhat similar rhodium-catalysed reaction does involve such a species.⁶ The reaction of alkynes with thallium(III) is complex, the

† It has been reported that phenylethyne is unreactive towards mercury(II) chloride in methanol.¹⁰ We did not find it so.

¹ R. O. C. Norman, W. J. E. Parr, and C. B. Thomas, *J.C.S. Perkin I*, 1976, 811.

² M. Kucherov, *Ber.*, 1884, **17**, 13.

³ R. J. Thomas, K. N. Campbell, and G. F. Hennion, *J. Amer. Chem. Soc.*, 1938, **60**, 718.

⁴ M. Micoque, N. M. Hung, and V. Q. Yen, *Ann. Chim. (France)*, 1963, **8**, 157.

⁵ W. L. Budde and R. E. Dessy, *J. Amer. Chem. Soc.*, 1963, **85**, 3964.

cases but gradually activity was lost and metallic gold precipitated out. In some cases comparable reactions were carried out with mercury(II) chloride.† The products, both ketonic and olefinic, were identical for the two metal oxidants but the yields were significantly higher with gold(III).

⁶ B. R. James and G. L. Rempel, *J. Amer. Chem. Soc.*, 1969, **91**, 863.

⁷ A. McKillop, O. H. Oldenzel, B. P. Swann, E. C. Taylor, and R. L. Robey, *J. Amer. Chem. Soc.*, 1973, **95**, 1296.

⁸ J. Jadot and M. Neuray, *Bull. Soc. roy. Sci. Liège*, 1961, **30**, 34, 52.

⁹ Sung Moon and W. J. Campbell, *Chem. Comm.*, 1966, 470; R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 771.

¹⁰ G. F. Dvorko and E. A. Shilov, *Ukrain. khim. Zhur.*, 1962, **28**, 833 (*Chem. Abs.*, 1963, **59**, 1449a).

Reaction proceeds with a high degree of regioselectivity in the case of the monosubstituted alkynes, consistent with the view that a considerable degree of carbocation character is developed in the transition state leading to the adduct. With oct-2-yne, however, there is little

TABLE 1

Products from the oxidation of alkynes (3-fold excess) by tetrachloroauric acid in methanol after 24 h under reflux

Alkyne	Products	Yields (%)	
		Gold(III) oxidation	Mercury(II) oxidation
$C_6H_{13} \cdot C \equiv CH$	$C_6H_{13} \cdot COMe$	180	<i>a</i>
$C_6H_{11} \cdot C \equiv CMe$	$C_6H_{13} \cdot COMe$	95	55
	$C_6H_{11} \cdot COEt$	95	45
$Pr^a C \equiv CPr^a$	$Pr^a COBu^a$	138	<i>a</i>
$PhC \equiv CH$ ^b	$PhCOMe$	570	454
	$PhCOEt$	35	5.1
$PhC \equiv CMe$	$PhCH_2 \cdot COMe$	15	1.6
	$PhCHCl \cdot COMe$	10	
<i>p</i> -MeO· C_6H_4 · $C \equiv CMe$	<i>p</i> -MeO· C_6H_4 · $COEt$	65	56
	$PhCH_2 \cdot COPh$	110	<i>a</i>

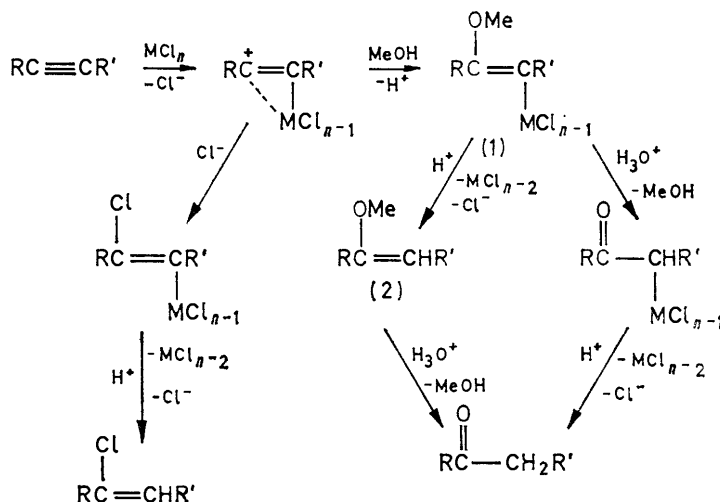
^a No mercury-catalysed reaction carried out. ^b Fifteen-fold excess of alkyne used.

selectivity with either oxidant; presumably there is little to choose between the abilities of methyl and *n*-pentyl to stabilise a positive centre. Perhaps more

between the aryl ring and the empty *p* orbital.¹¹ None of these studies, however, included substrates possessing electron-rich substituents on the β -carbon atom (*i.e.* that vinylic carbon atom adjacent to the positive centre) and it may be that such groups radically alter the situation. Indeed, Hassner showed that reaction of 1-phenylpropyne with iodine azide leads solely to 2-azido-1-iodo-1-phenylpropene,¹² whereas on bromination¹³ the electrophile attaches itself exclusively to C-2. He explained this by invoking stabilisation *via* a cyclic iodonium ion in which conjugation of the aromatic ring and the double bond was still complete, such neighbouring-group participation being substantially reduced for a bromine atom. By analogy, gold(III) and mercury(II) must both interact significantly with the carbocation centre.

The only other point deserving of comment is that the introduction of a second substituent onto the acetylene group in an arylalkyne greatly decreases its reactivity. It would be tempting to invoke 'steric hindrance' to explain this were it not that for aliphatic alkynes there is no evidence of such an effect.

The close analogy between the products of gold(III)- and mercury(II)-catalysed reaction suggests a common mechanism. That this is not simply an acid-catalysed



SCHEME 1

surprisingly, both sites in 1-phenylpropyne are attacked. This might be explicable if stabilisation of the intermediate carbocation were greater when the aromatic ring remains conjugated to the bonding π -electrons rather than to an empty *p* orbital. However, introduction of an electron-donating substituent into the *para*-position greatly favours electrophilic attack on C-2, so that in this case mesomeric interaction of the aryl group evidently acts to stabilise the positive centre. In a number of solvolytic studies of vinyl cations it has been claimed that there is substantial orbital overlap

¹¹ L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, 1968, **90**, 7282; R. J. Hargrove, T. E. Dueber, and P. J. Stang, *Chem. Comm.*, 1970, 1614; C. A. Grob and R. Nussbaumer, *Helv. Chim. Acta*, 1971, **54**, 2528.

process was demonstrated by omitting the metal compound but including an equivalent amount of hydrochloric acid. No ketones were observed. The formation of both possible ketones from 1-phenylpropyne likewise eliminates an acid-catalysed process.¹⁴ We therefore propose Scheme 1 to account for the observed products. Whether the intermediate adduct (1) undergoes acid-catalysed hydrolysis before displacement of the metal, or the vinylic ether (2) is the immediate

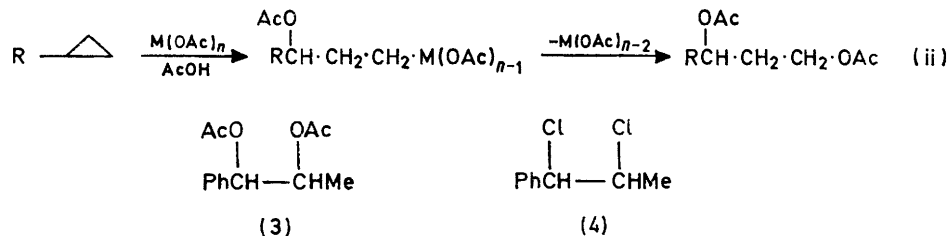
¹² A. Hassner, R. J. Isbister, and A. Friederang, *Tetrahedron Letters*, 1969, 2939.

¹³ J. A. Pincock and K. Yates, *J. Amer. Chem. Soc.*, 1968, **90**, 5643.

¹⁴ D. S. Noyce and M. D. Schiavelli, *J. Org. Chem.*, 1968, **33**, 845.

precursor of the major product, we cannot be sure. Certainly small amounts of (2) could be detected from a number of the reactions and α -methoxystyrene was almost entirely hydrolysed to acetophenone under the work-up conditions.

Cyclopropanes.—Oxidation of cyclopropanes by lead(IV), thallium(III), or mercury(II) results in very similar products, namely, 1,3-organometallic adducts which, in the case of the first two metals, undergo carbon-metal bond cleavage [e.g. reaction (ii)].¹⁵ Since phenylcyclopropane is one of the more extensively studied substrates for such oxidations we chose this compound for our gold(III) investigations. Reaction with tetrachloroauric acid in methanol or in water led to little conversion of the cyclopropane but, surprisingly in view of the earlier results,¹ reaction in acetic acid proceeded smoothly. However, the products were not the expected 1,3-adducts but instead, as deduced from g.l.c.-mass spectrometry, were 1,2-addition products. Four of them were identified, by comparison with authentic samples, as the two diastereoisomers of the diacetate (3) and the dichloride (4).



A partial explanation of this was provided when it was found that, amongst the more volatile components of the reaction product, was a substantial quantity of *trans*-1-phenylpropene, from which the above 1,2-adducts can be derived.^{1,*} Gold(III) therefore appears to have the unexpected ability to isomerise cyclopropanes to olefins. We demonstrated that a similar situation held when pentylcyclopropane was the substrate. The observed long retention time products were 1,2-adducts of oct-2-ene, as evidenced by comparison with authentic compounds and by g.l.c.-mass spectrometry.

When the reaction of phenylcyclopropane was carried out in acetic [²H]acid the mass spectrum of the olefin indicated the partial incorporation of one deuterium atom into the olefin. Control experiments demonstrated that no isomerisation occurred in the absence of gold(III) and that *trans*-1-phenylpropene does not exchange protons in acetic [²H]acid. Since terminal olefins can undergo isomerisation to internal alkenes in the presence of palladium(II),¹⁶ we subjected 3-phenylpropene to the

* Oxidation of the alkene under identical conditions led to the same products in similar, though not identical, ratios. (The production and subsequent reaction of some *cis*-1-phenylpropene would ensure that the ratios were dissimilar.)

¹⁵ R. J. Ouellette, R. D. Robins, and A. South, *J. Amer. Chem. Soc.*, 1968, **90**, 1619; A. South and R. J. Ouellette, *ibid.*, p. 7064; R. J. Ouellette, D. Miller, A. South, and R. D. Robins, *ibid.*, 1969, **91**, 971.

reaction conditions but no 1-phenylpropene (or products therefrom) were found. It therefore appears that gold(III) brings about direct isomerisation to the conjugated olefin.

The only related reaction reported appears to be the palladium(II) chloride-catalysed isomerisation of phenylcyclopropane in aqueous bis-(2-methoxyethyl) ether to give, *inter alia*, *trans*-1-phenylpropene.¹⁷ However, the mechanism proposed in that study involves initial formation of 3-phenylpropene, which cannot be the case here. It also relies on an elimination-addition sequence involving a hydridopalladium species which, although not inconceivable for gold(III), would be without precedent.

In order to find the position of the deuterium in the 1-phenylpropene, this product was isolated by preparative g.l.c. and subjected to detailed ¹H n.m.r. analysis. Successively replacing the protons by deuterium in a computer-simulated spectrum, we obtained the best fit to the observed spectrum for a mixture of 55% 1-phenyl[3-²H₁]propene and 45% unlabelled 1-phenylpropene. Thus deuterium is incorporated specifically at

the methyl carbon atom, the incomplete labelling probably being due to the presence of protons from the hydrated gold(III) reagent. The most likely isomerisation route is one involving decomposition of a gold(III)-cyclopropane complex with loss of a proton and formation of an allylic gold compound (Scheme 2a); proto-deauration of this would lead to the observed result. An alternative process involving the standard ring opening (Scheme 2b) seems unlikely since the resultant carbocation ought to react with nucleophiles to give 1,3-adducts, for which there is no evidence, despite our attempts to trap such a species by the addition of methanol.

Aromatic Substrates.—The reaction of arenes with gold(III) chloride was first noted some 40 years ago by Kharasch and Isbell.¹⁸ They reported that, in an excess of benzene, gold(I) chloride and chlorobenzene are formed, but that the timely addition of ether enabled them to isolate phenylgold(III) dichloride. When tetrachloroauric acid was used no reaction occurred, a fact we may now attribute to the lack of a vacant fourth co-ordination site on the metal in this compound. With

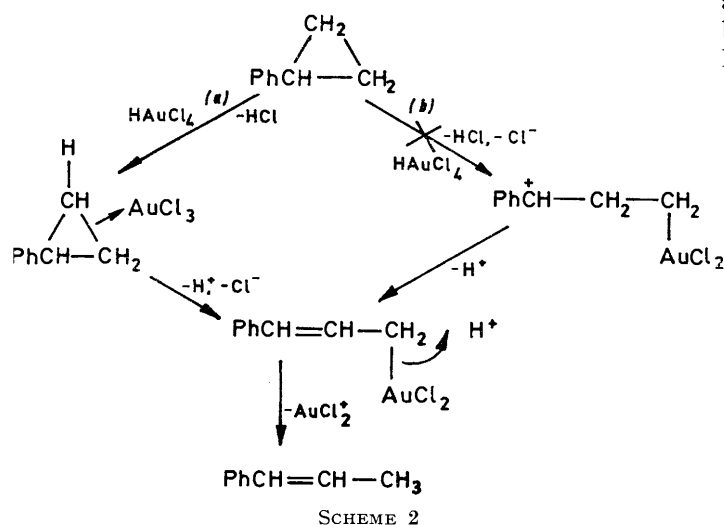
¹⁶ B. I. Cruickshank and N. R. Davies, *Austral. J. Chem.*, 1973, **26**, 2635.

¹⁷ R. J. Ouellette and C. Levin, *J. Amer. Chem. Soc.*, 1971, **93**, 471.

¹⁸ M. S. Kharasch and H. S. Isbell, *J. Amer. Chem. Soc.*, 1931, **53**, 3053.

other arenes the rate of reaction shows all the characteristics of an electrophilic substitution, and auration may thus be compared with mercuration. The arylgold(III) compounds are, however, reported to be much less stable than their mercury(II) analogues,¹⁸ so that chlorobenzene could be formed *via* an organometallic intermediate. Tempting as this is, alternative ways for the introduction of chlorine can be envisaged. In particular, a gold(III)-catalysed chlorination sequence [cf. thallium(III)-catalysed bromination¹⁹] following dissociation to chlorine and gold(I) is a possibility.²⁰

In order to check whether the formation of chlorobenzene does involve electrophilic auration we attempted to duplicate the earlier work. In this we failed.* In view of the absence of other reports of arylgold(III) dichlorides over the last 40 years, and the recent claim by Parkin to have characterised the first such compound, which even so required to be stabilised by electron-donating ligands such as pyridine,^{21,†} the earlier claim should be treated with caution.

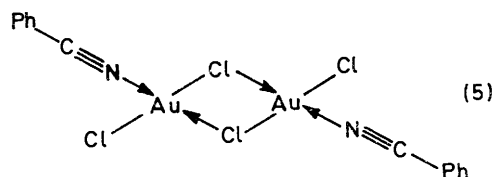


We did isolate from an arene one compound containing gold(III). Benzonitrile gave a solid which melted with decomposition. Kharasch²³ believed that this compound was a gold-substituted benzene derivative. However, the experimental evidence cited, other than microanalysis, where differences would be minimal, is more consistent with a dimeric species in which the nitrogen of the cyanide group is co-ordinated to the gold, e.g. structure (5). In support of this view we found that the ¹H n.m.r. spectrum (solvent CD₃CN) was

* It is claimed that, on addition of anhydrous gold(III) chloride to an excess of benzene, a red solution is obtained which, shortly, turns brown and, a few minutes later, yields a bright yellow precipitate. If ether is added as soon as the brown colour is observed a yellow solution results from which phenylgold(III) dichloride can be isolated. Our main problem, other than the economic one of scale, was our inability to dissolve more than a small portion of the gold(III) chloride before the appearance of the brown colour.

† There is an earlier note²² in which the n.m.r. parameters of C₆H₅AuBr₂.PPh₃ are cited in a Table. However, the compound is not mentioned in the text and there are no experimental details.

virtually identical with that of free benzonitrile (the solvent may well displace benzonitrile from the complex) and the mass spectrum likewise showed no evidence of a carbon-gold bond: the only ions observed were assignable to benzonitrile.



The final products of reaction of gold(III) chloride with aromatic substrates were investigated. The only compounds identified were chlorinated benzene derivatives, and the isomer distribution is set out in Table 2 together with those from some related systems. The results compare well with the ones obtained from thallation, but are dissimilar from those of direct chlorination, the low yield of *ortho*-isomer having been attributed in the former case to steric interaction between the substituent and the bulky electrophile.^{24,25} It might be argued that direct chlorination catalysed by

TABLE 2

Isomer distributions from the reactions of aromatic substrates with gold(III) chloride and related reagents

Substrate	Isomer distribution (<i>o</i> : <i>m</i> : <i>p</i>)		
	AuCl ₃ ^a	Cl ₂ ^a	Tl(O ₂ CCF ₃) ₃
PhMe	19 : 0 : 81	59 : 0.5 : 40 ^b	9 : 0 : 91 ^c
PhOMe	11 : 0 : 89	63 : 2 : 35 ^d	11 : 2 : 87 ^e
PhCl	10 : 0 : 90	32 : 0 : 68 ^f	7 : 0 : 93 ^e
		42 : 3 : 53 ^d	23 : 0 : 77 ^e

^a Products: aryl chlorides. ^b H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 5175. ^c Thalliated products analysed as iodides (ref. 24). ^d Iron(III) chloride present as catalyst (ref. 26). ^e Thalliated products analysed as nitro-compounds (ref. 25). ^f D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 1961, 3604. ^g L. M. Stock and F. W. Baker, *J. Amer. Chem. Soc.*, 1962, **84**, 1661.

a Lewis acid could also show a greater preference for the *para*-position, but the presence of iron(III) chloride seems to make little difference to the isomer distribution²⁶ (cf., however, Tl^{III}-catalysed bromination¹⁹). We therefore prefer as the mode of formation of aryl chlorides from gold(III) oxidation a metallation process followed by heterolysis of the highly labile arylgold(III) dichloride intermediate.

¹⁹ A. McKillop, D. Bromley, and E. C. Taylor, *J. Org. Chem.*, 1972, **37**, 88.

²⁰ 'Nouveau Traité de Chimie minérale,' ed. P. Pascal, Masson, Paris, 1957, vol. 3, p. 748.

²¹ K. S. Liddle and C. Parkin, *J.C.S. Chem. Comm.*, 1972, 26.

²² L. G. Vaughan and W. A. Sheppard, *J. Organometallic Chem.*, 1970, **22**, 739.

²³ M. S. Kharasch and T. M. Beck, *J. Amer. Chem. Soc.*, 1934, **56**, 2057.

²⁴ A. McKillop, J. D. Hunt, M. J. Zelesko, J. S. Fowler, E. C. Taylor, G. McGillivray, and F. Kienzle, *J. Amer. Chem. Soc.*, 1971, **93**, 4841.

²⁵ B. Davies and C. B. Thomas, *J.C.S. Perkin I*, 1975, 65.

²⁶ G. A. Olah, S. J. Kuhn, and B. A. Hardie, *J. Amer. Chem. Soc.*, 1964, **86**, 1055.

EXPERIMENTAL

Most of the general methods employed in this study have been detailed previously (ref. 1 and references therein). Likewise many of the substrates and the products required were available from earlier work. Most of the rest were commercially available.

Other Materials.—Oct-1-yne. Iron(III) nitrate (0.3 g) was added to liquid ammonia (700 ml) at -35°C , followed by sodium (1 g). The solution was then stirred until no blue coloration remained, more sodium (26.6 g) was added over 1 h, and ethyne was passed through the solution for 4 h. The solution was cooled to -50°C and 1-bromohexane (125 g) was added over 1 h. The solution was stirred for 4 h at -25°C , and ammonium chloride (20 g) was added, followed by water (300 ml). The organic layer was separated, washed with ice-hydrochloric acid (1:1 v/v), dilute sodium carbonate solution, and water, and dried (MgSO_4). Removal of the solvent and distillation gave oct-1-yne (50 g, 60%), b.p. $126-128^{\circ}$ (lit.,²⁷ 126°).

1-Phenylpropyne. 1-Phenylpropan-2-one (65 g) was added dropwise over 1 h to phosphorus pentachloride (124 g), and the mixture was refluxed for 4 h. The volatile components were removed at atmospheric pressure and the residue was distilled to give a fraction, b.p. $98-118^{\circ}$ at 20 mmHg, composed of isomeric chloroalkenes. This was added in portions to a refluxing solution of potassium hydroxide (45 g) in ethanol (100 ml) over $1\frac{1}{2}$ h. After a further 4 h under reflux the solution was cooled and poured into water, and the ethereal extracts were washed and dried (MgSO_4). Removal of the solvent and distillation of the residue afforded 1-phenylpropyne (15.2 g, 27%), b.p. $82-84^{\circ}$ at 18 mmHg (lit.,²⁸ $80-82^{\circ}$ at 17 mmHg); τ 2.80br (5 H, s, ArH) and 8.01 (3 H, s, CH_3).

1-p-Methoxyphenylpropyne. The same method was used as for 1-phenylpropyne, starting from 1-*p*-methoxyphenylpropan-2-one. 1-*p*-Methoxyphenylpropyne had b.p. $126-128^{\circ}$ at 15 mmHg (lit.,²⁹ $115-117^{\circ}$ at 9 mmHg).

Pentylcyclopropane. This was prepared from hept-1-ene by the method of Simmons and Smith,³⁰ and purified by preparative g.l.c.; τ 8.4—8.9 (8 H, aliphatic envelope), 8.9—9.3 (4 H, m, CH_2 and ring CH), and 9.4—9.75 (4 H, m, ring [CH_2]₂).

²⁷ 'Heilbron's Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

²⁸ J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, 1966, **88**, 2213.

Ethyl *p*-methoxyphenyl ketone. To a stirred solution of anisole (22 g) in carbon disulphide (100 ml), aluminium chloride (60 g) was added, followed by propanoyl chloride (11.6 g) over 1 h. The resultant mixture was refluxed for 2 h, cooled, and poured onto crushed ice-concentrated hydrochloric acid, and the ethereal extract was washed with dilute sodium hydrogen carbonate solution and water and dried (MgSO_4). Removal of the solvent and distillation gave ethyl *p*-methoxyphenyl ketone, b.p. $68-70^{\circ}$ at 15 mmHg (lit.,²⁸ $145-147^{\circ}$ at 14 mmHg).

Benzonitrile-Gold(III) Complex.—Anhydrous gold(III) chloride (0.75 g) was added to benzonitrile (2 ml) and the mixture was left for 2 h. The liquid was decanted off and diluted with dry ether. The precipitate, filtered off and dried *in vacuo*, had m.p. $163-166^{\circ}$ (decomp.) [lit.,²⁴ 168° (decomp.)] and ¹H n.m.r. and mass spectra identical with those of benzonitrile.

Oxidation Procedures.—Alkynes. The alkyne (0.005 mol) was added to a solution of tetrachloroauric acid (0.000 33 mol) in methanol (10 ml). The mixture was refluxed for 24 h, cooled, and poured into water, and the ethereal extracts were washed with dilute sodium hydrogen carbonate and water and dried (MgSO_4). Most of the solvent was removed, a suitable standard added, and the product analysed by g.l.c.—mass spectrometry.

The same general procedure was used for the reaction of mercury(II) chloride with alkynes.

Cyclopropanes. The cyclopropane (0.1 g) was added to a solution of tetrachloroauric acid (0.1 g) in acetic acid (10 ml). The mixture was heated at 100°C for 24 h, cooled, poured into water, and worked up and analysed in the usual way. Separation of the 1-phenylpropene after deuteration was achieved by preparative g.l.c.

Aromatic Substrates.—In attempting to isolate arylgold(III) dichlorides, the procedure of Kharasch was employed.¹⁷ In the studies of the oxidation products the arene (0.002 mol) was added to a solution of gold(III) chloride (0.000 33 mol) in nitromethane (10 ml); the solution was refluxed for 24 h, cooled, and worked up and analysed in the usual way.

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

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²⁹ G. I. Hobday and W. F. Short, *J. Chem. Soc.*, 1943, 609.

³⁰ H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 4256.