On a Mechanism for the *trans*-Addition of Alkylmagnesium and Alkyl-rhodium Derivatives to Diphenylacetylene

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The reaction of diphenylacetylene with tris(triphenylphosphine)rhodium bromide yields 1,2-diphenylpropene mostly as the *trans*-isomer. When reactions are terminated with D_2O it is shown that *trans*-1,2-diphenylpropene is deuteriated at the vinylic position and at the *ortho*-position of the aromatic ring adjacent to the methyl group. The *cis*-isomer is deuteriated at the vinylic position only. These results offer an explanation of the mechanism of *trans*-addition in this case. Possible implications for other cases of *trans*-addition are discussed.

THE addition reactions of acetylenes to organometallic complexes often result in insertion yielding vinylmetal complexes or addition products [1] with *cis*- and *trans*-configurations. While the *cis*-configuration is expected for most insertion processes, *trans*-additions have often presented problems of interpretation, especially when observed as the dominant result. In some reports *cis*- and *trans*-adducts were shown to isomerize.[2,3] Others describe reactions of metal complexes from both sides of an alkyne.[4] Others claim an inversion around the vinylic double bond of an adduct during protonolysis [5] or else aided by electron donation from the metal in a vinylmetal compound.[6,7] *trans*-Intermediates with special structural features have also been found as in additions to dimethyl acetylenedicarboxylates [8] or in hydrogenation of diphenylacetylene through an allene intermediate.[9] Sometimes, *trans*-addition to acetylenes occurs with high yields for no apparent reason while similar reactions yield *cis*-products,[5,10-19] *e.g.*, aluminoalkylations of alkynes.[20,21] Many proposed explanations are difficult to prove [5,9] and the routes by which *trans*-additions occur still pose considerable mechanistic problems. In this study we present results which offer a rationalization for *trans*-addition and which, we believe, have implications for other such cases.

RESULTS

Diphenylacetylene was allowed to react with tris(tri-phenylphosphine)rhodium bromide [(Ph₃P)₃RhBr] and methylmagnesium bromide as described earlier.[5] The main addition product was *trans*-1,2-diphenylpropene, with some *cis*-isomer. The *trans*:*cis* ratio was usually 10—

14 : 1 and constant throughout the reaction. It has already been demonstrated that products form only after hydrolysis and incorporate deuterium atoms at the vinylic position of the propene, when D_2O is used.[5] Detailed analysis now shows that *cis*-1,2-diphenylpropene contains a single deuterium atom, at the vinylic position, but the *trans*-isomer contains mostly two, to some extent even three, deuterium atoms and almost no molecules with a single deuterium atom (Scheme). The presence of triphenyl-phosphine and triphenylphosphine oxide released from the rhodium complex interfered with some of the tests. Analysis was therefore carried out first with the crude mixture of organic products, involving the least work-up possible, in order to avoid any unpredictable changes in deuterium atom distribution. Secondly, *trans*-1,2-diphenyl-propene was separated from phosphine and phosphine oxide and the crystalline compound analysed. Thirdly, *trans*-1,2-diphenylpropene was ozonolysed to yield aceto-phenone and benzaldehyde, for the final location of aromatic deuterium atoms. Combined g.l.c.–m.s. results are presented in Table 1.

The clusters for the molecular and the parent peaks indicate the extent of deuterium incorporation. The *cis*-isomer is mostly monodeuteriated with some dideuteriation while the *trans*-isomer is dideuteriated. The extent of mono- and zero deuteriation in the *trans*-isomer is uncertain but small, as confirmed by other results (see below). Fractionation in the gas chromatograph of deuteriated and non-deuteriated compounds is accounted for. Some complications arise in regard to intensity measurements. The standard compounds which were independently prepared (Table 1) show an $(M + 1)^+$ ion which has a higher intensity than that expected for a C_{15} hydrocarbon (12.9 relative to 65.7% of the largest peak for M^+ for the *trans*- and 15.7 relative to 71.1% for M^+ for the *cis*-isomer, the expected values being 9.85 and 10.9% respectively). This holds for

[1] R. F. Heck, ' Organotransition Metal Chemistry,' Academic Press, New York, 1974, p. 108.
[2] J. G. Duboudin and B. Jousseaume, *J. Organometallic Chem.*, 1975, **96**, C47.
[3] M. Michman and H. H. Zeiss, *J. Organometallic Chem.*, 1968, **15**, 139.
[4] C. E. Castro and R. D. Stephens, *J. Amer. Chem. Soc.*, 1964, **86**, 4358.
[5] M. Michman and M. Balog, *J. Organometallic Chem.*, 1971, **31**, 395.
[6] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 106.
[7] D. W. Hart and J. Schwartz, *J. Organometallic Chem.*, 1975, **87**, C11.
[8] H. C. Clark and K. E. Hine, *J. Organometallic Chem.*, 1976, **105**, C32.
[9] P. Abley and F. McQuillin, *Chem. Comm.*, 1969, 1503.
[10] B. L. Booth and R. G. Hargreaves, *J. Organometallic Chem.*, 1971, **33**, 365; *J. Chem. Soc.* (*A*), 1970, 308.
[11] D. M. Barlex, R. D. W. Kemmit, and G. W. Littlecott, *Chem. Comm.*, 1969, 613.

[12] P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, 1962, **1**, 511.
[13] K. Tamao, M. Zembayashi, Y. Kiso, and M. Kumada, *J. Organometallic Chem.*, 1973, **55**, C91.
[14] B. F. G. Johnson, J. Lewis, J. D. Jones, and K. A. Taylor, *J.C.S. Dalton*, 1974, 34.
[15] P. B. Tripathy, B. W. Renoe, K. Adzamli, and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1971, **93**, 4406.
[16] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Comm.*, 1970, 1333.
[17] B. L. Booth and A. D. Lloyd, *J. Organometallic Chem.*, 1972, **35**, 195.
[18] R. M. Laine and P. C. Ford, *J. Organometallic Chem.*, 1977, **124**, 29.
[19] K. S. Wheelock, J. H. Nelson, J. D. Kelly, H. B. Jonassen, and L. C. Cusachs, *J.C.S. Dalton*, 1973, 1457.
[20] E. F. Magoon and L. H. Slaugh, *Tetrahedron*, 1967, **23**, 4509.
[21] H. Hoberg and V. Gotor, *J. Organometallic Chem.*, 1977, **127**, C32.

the $^2H_1$ and $^2H_2$ components and $(M - 1)^+$ ions and since the value of the isotope effect is unknown, a reliable calculation of the cluster is not possible. However, the methyl group
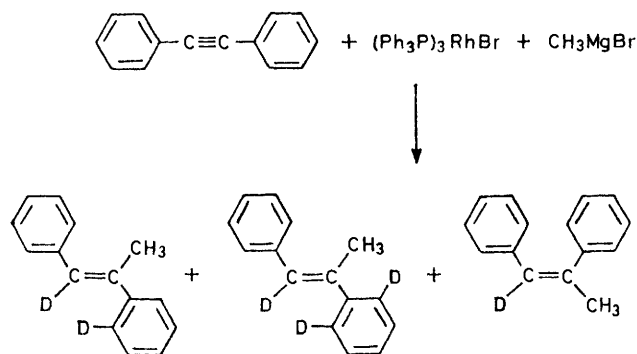
Scheme Alkylation of diphenylacetylene followed by hydrolysis with D^+–D_2O

is not deuteriated as shown by the clusters of $(M - 15)^+$, which show the same deuterium pattern as the molecular ions.

103 and 104. Thus only the ring adjacent to the methyl group of the propene is deuteriated (Scheme). Apparently, dideuteriation of the aromatic ring is significant too. The mass spectra of benzaldehyde and acetophenone show little excessive $(M + 1)^+$ for the molecular ions M^+, and the extent and pattern of overall deuteriation is clearer here than with the propene.

In order to determine the position of the aromatic deuterium atoms, deuteriated acetophenone and benzaldehyde were separated by sodium hydrogensulphite. The 100 MHz n.m.r. spectrum of acetophenone from the reaction shows a reduction of ca. 60% in the intensity of the signal at δ 7.76 for ortho protons,[24, 25] accompanied by considerable collapse of spin couplings in the region of the meta–para-absorption. The presence of some ortho-protium in the deuteriated acetophenone must of course be expected.

DISCUSSION

The results offer a rationalization for the formation of cis- and trans-1,2-diphenylpropene by separate pathways, assuming that addition of water or deuterium oxide causes cleavage of carbon–metal bonds and is

TABLE 1

1,2-Diphenylpropene from reaction of PhC≡CPh, $(Ph_3P)_3RhBr$, and CH_3MgBr with (A)H_2O; (B)D_2O

m/e	trans (A)	trans (B)	cis (A)	cis (B)	Synthetic	(B) Isolated
197		34.7		14.7		43.75
196		67.6	(2.9)	32.8		83.97
195	12.9	26.8	15.7	47.0	21.30	31.25
194 M^+	65.7	11.1	71.1	38.2	97.90	10.00
193 $(M - H)^+$	15.0		21.9	13.2	32.30	
182		44.9		17.6		45.00
181		100		44.1	3.00	100
180	21.4	75.0	18.7	100	27.70	75.00
179 $(M - CH_3)^+$	100	35.6	100	73.5	100	38.75
178 $(M - CH_3 - H)^+$	70.0	9.3	63.4	30.8	80.80	25.00
177	10.0		9.5	15.3		
79					1.50	8.10
78					5.50	11.90
77					24.70	15.00

The mass spectrum of the isolated trans-diphenylpropene confirms these results. The extent and pattern of deuteriation are not changed by the isolation procedures. Considerable aromatic deuteriation is observed around m/e 77. The n.m.r. spectrum (100 MHz) of trans-diphenyl-propene shows the absence of deuterium in the vinylic methyl group (no loss of intensity at δ 2.25) and practically complete deuteriation at the position of the vinylic hydrogen (complete disappearance of absorption at δ 6.77). The absence of ' allylic scrambling ' between the methyl group protons and that in the vinylic position [22] which might occur with homogeneous catalysis [23] is noteworthy.

Ozonolysis of the deuteriated trans-1,2-diphenylpropene yielded equal amounts of benzaldehyde and acetophenone (Table 2). Benzaldehyde is exclusively deuteriated at the carbonyl carbon. Practically no aromatic deuterium is present as only a small peak at m/e 78 (ca. 11%) is detected. Small amounts of non-deuteriated benzaldehyde are probably present as well. Acetophenone shows extensive deuteriation and some dideuteriation of the aromatic ring but none at the methyl group as no ions are present at m/e

thus an indicator of their existence. Indeed, formation of the addition products is not observed in this reaction

TABLE 2

Mass spectra of benzaldehyde and acetophenone from ozonolysis of deuteriated trans-1,2-diphenylpropene

m/e	Commercial benzaldehyde	Product of ozonolysis	Commercial acetophenone	Product of ozonolysis
122				21.1
121			2.6	19.7
120			25.7 (M^+)	21.1
108				
107	8.20	67.80		44.2
106	94.5 (M^+)	50.85	8.6	79.0
105	94.0	89	100 $(M - CH_3)^+$	100
104				
79				43.5
78	14.0	25.4	9.4	61.9
77	100	100	75.4 $(C_6H_5)^+$	78.2

unless it is followed by hydrolysis.[5] Obviously, mono-deuteriated cis-isomer is not formed from the dideuteriated trans-isomer. The opposite cannot be ruled out.

[22] J. Powell and A. W. C. Chan, J. Organometallic Chem., 1972, 35, 203, cf. also ref. 1, p. 227.
[23] M. Michman and H. H. Zeiss, J. Organometallic Chem., 1970, 25, 167; cf. ref. 3.
[24] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, NMR Spectra Catalogue, Varian, Palo Alto, 1962, Spectrum No. 192.
[25] W. W. Simons and M. Zanger, ' The Sadtler Guide to NMR Spectra,' Sadtler Res. Inc., Philadelphia, 1972, pp. 367—372 for similar types of ortho-protons.

In spite of several possibilities for hydrogen–deuterium scrambling such as metallation of the phosphine ligands or repeated metallation of the diarylacetylene (see below), interference by such side reactions is not considerable.

Formation of the *cis*-isomer can be envisaged as an insertion into a metal (rhodium or magnesium)–methyl bond through a four-centred intermediate. Electrophilic hydrolysis by aqueous acids is expected to occur with retention of configuration at the metal–carbon bond to yield a *cis*-product. The yield of this isomer is very small. It was isolated by g.l.c. and shown to be deuteriated at the vinylic position by i.r. and n.m.r. measurements.[5]

Results for the *trans*-isomer suggest the following sequence. Diphenylacetylene, a linear molecule, complexes to the rhodium compound.[26] In the course of the addition to the triple bond the latter changes into the sp^2 geometry as in the Figure, in which the organic
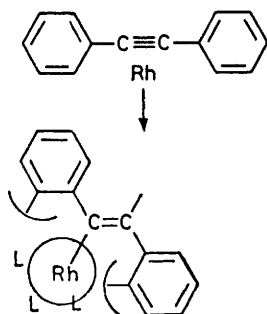
Transformation from a linear π complex of a 1,2-diarylalkyne to the *trans*-form of a σ complex

bond lengths and angles are drawn to scale. Whatever the exact radius of the rhodium atom in the complex, its centre is nearer to the *ortho*-positions of the ring adjacent to the position of alkylation. Ring metallation would then become a driving force for the formation of this transoid configuration and stabilize the product. Ring metallation [27] is very common with phosphine ligands, but is novel in the fashion described here between diphenylacetylene and a metal centre. Metallation of azobenzene complexes [28] is perhaps the closest analogy. The phenomenon of metallation of both *ortho*-positions of a given ring has also been reported with phosphines [29] and has not yet been fully explained. It is, however, easy to appreciate why the formation of the *trans*-isomer is so much preferred. Conversely, cases where such metallation is not possible will not necessarily result in preferred *trans*-addition. Some examples from the literature may be suggestive. The complex Pt(RC≡CR)-(Ph₃P)₂ was reported to react with trifluoroacetic acid yielding *cis*-adducts when R was the trifluoromethyl group and *trans*-stilbene when R was phenyl.[10] In another example RhH(CO)(Ph₃P)₃ yielded a *cis*-vinyl complex with hexafluorobutyne but *trans*-stilbene with diphenylacetylene.[17] Still it is not necessary for diaryl-

acetylene that metallation will always be observed (see below).

There remains the question of the initial attack on the triple bond. We maintain that for the description in the Figure to be realized, it is best to regard the actual alkylation as occurring by an outside attack, *i.e.* by the Grignard reagent which is present in large excess. Previous work [5] suggests that such nucleophilic attack is catalysed by complexation of alkyne to the rhodium complex. Methyltris(triphenylphosphine)rhodium, formed by the reaction of methylmagnesium bromide and tris(triphenylphosphine)rhodium bromide under these conditions, is not reactive below 130 °C.[5] The reaction path described here is much simpler than others proposed for *trans*-additions,[5,9] and fits commonly accepted mechanistic concepts.

Alternatively, *cis–trans*-isomerization of a vinylic adduct can be facilitated by the adjacent metal, which could donate a negative charge to the π system and enable rotation around the double bond. These possibilities have been put forward by Hart and Schwartz [7] and by Blackmore, *et al.*,[6] with reference to intramolecular hydrogen transfer reactions, in which a reaction from outside the complex was unlikely. However, in this case too, metallation as in the Figure would explain the strong preference for the *trans*-isomer. Isomerizations of this type have been claimed to be enhanced by phosphine ligands in the metal complex and indeed this offers an intriguing explanation for the observation that the rhodium reagent which we described here gives mostly *trans*-adducts while methylmagnesium bromide and rhodium(III) chloride yields *cis*-adducts.[5] Rhodium(III), with no phosphine ligands, would certainly be a weak donor of electrons by comparison with rhodium(I) surrounded by three phosphine ligands; *cis–trans*-isomerization would be less likely with rhodium(III) chloride.

It should be mentioned that our proposed mechanism is not always applicable. An apparently very similar reaction of diphenylacetylene with methyltris(triphenylphosphine)cobalt yielded likewise, *trans*-1,2-diphenylpropene which incorporated no deuterium whatever.[30] Either the cobalt–carbon bonds are cleaved by hydrogen donors from other sources (phosphine, solvent) before hydrolysis, or another mechanism applies altogether. For example, a different mode of complexation of diphenylacetylene with a rhodium compound has recently been suggested by Rausch *et al.*[31]

It should also be mentioned that *cis*- and *trans*-stilbene form in small yields in this reaction, with incorporation of deuterium.[5] The source of hydrogen for these products is not yet clear.

EXPERIMENTAL

Materials.—Solvents were distilled and dried before use. Experiments were carried out under argon or nitrogen

[26] J. T. Mague and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1736.
[27] M. I. Bruce, *Angew. Chem. Internat. Edn.*, 1977, **16**, 73.
[28] J. P. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, 1963, **85**, 1544.
[29] G. W. Parshall, *Accounts Chem. Res.*, 1975, **8**, 113.
[30] M. Michman, B. Steinberger, and S. Gershoni, *J. Organometallic Chem.*, 1976, **113**, 293.
[31] J. L. Todd, J. R. Wilkinson, M. D. Rausch, S. A. Gardner, and R. S. Dickson, *J. Organometallic Chem.*, 1975, **101**, 133.

except when otherwise stated. Deuteriated compounds were compared with authentic non-deuteriated compounds by all the analytical methods used. *cis*- and *trans*-1,2-diphenylpropene were prepared as in ref. 3.

Instruments.—I.r. spectra were taken with a Perkin-Elmer 337 spectrophotometer. N.m.r. spectra were taken on a Varian HR-100 instrument. Mass spectra were taken with Varian GCMS MAT-111 and Varian MAT-311 spectrometers (ionization at 70 eV).

Reaction of Tris(triphenylphosphine)rhodium Bromide and Methylmagnesium Bromide with Diphenylacetylenes.—The reaction of tris(triphenylphosphine)rhodium bromide and methylmagnesium bromide with diphenylacetylene was carried out as previously described.[5] Freshly distilled acetic anhydride was hydrolysed with deuterium oxide, $v_{max.}$ 2 600 (O–D) and 1 715 cm^{-1} (C=O); no absorption at 3 500 cm^{-1} (O–H). This acid was used to terminate reactions. After hydrolysis, the hexane extract was chromatographed over silica gel and analysed by g.l.c.–m.s. Mass spectral readings were taken at several points of each peak during g.l.c. Inconsistencies in relative intensity were observed in the marginal regions, but measurements taken at the upper ¾ area of each peak gave consistent results, within 5% of the values presented in Table 1.

trans-1,2-Diphenylpropene from this eluant was isolated by adding chloroform and a 0.1N-iodine solution until a persistent yellow colour was obtained. [The iodine solution was prepared by adding iodine (0.32 g) to potassium iodide (0.5 g) in water (1 ml), and making up to 25 ml.] After several minutes the mixture was chromatographed over silica gel with hexane. The first fraction contained

trans-1,2-diphenylpropene which was recrystallized from ethanol. Triphenylphosphine was converted into triphenylphosphine oxide [32] which, as shown by t.l.c. tests, is not eluted by further chromatography on silica or alumina.

Ozonolysis of 1,2-*Diphenylpropene.*—Ozone was bubbled through *trans*-1,2-diphenylpropene (30 mg, 0.4 mmol) in dry methylene chloride (50 ml) cooled in a dry ice–acetone bath. After 35 min, the system was flushed with nitrogen and excess (1.68 g, 11.2 mmol), solid sodium iodide added together with acetic acid (1.68 ml). The slurry was left overnight with stirring. Organic products were collected, washed with 5% sodium hydrogencarbonate and 10% sodium thiosulphate and dried (Na$_2$SO$_4$). G.l.c. on a 20% Carbowax column showed a 1 : 1 mixture of benzaldehyde and acetophenone. G.l.c.–m.s. analysis was carried out on silicone SE 30 columns.

Isolation of Acetophenone.—An aqueous ethanol solution of sodium hydrogensulphite [33] was added (0.2 ml) to a vial containing ozonolysis products (*ca.* 80 mg), left overnight, and extracted with ether (2 ml). Decantation and evaporation left a concentrated sample of acetophenone. The procedure was repeated three times with freshly prepared hydrogensulphite solution until no benzaldehyde was observed in the n.m.r. spectra of the isolated acetophenone.

[32] O. Lorenz, *Analyt. Chem.*, 1965, **37**, 101.
[33] A. Vogel, ' Textbook of Practical Organic Chemistry,' Longman, London, 1957, 3rd edn., p. 331.