Rhodium(I)-catalysed Dimerisation of Terminal Acetylenes at Ambient Temperature and Pressure

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Oct-1-yne is smoothly dimerised by the complex [RhCl(PPh₃)₃] at room temperature to give the branched chain isomer, 7-methylenepentadec-8-yne, as the main product. Other alkynes behave similarly. Phenylacetylene gives E-1,4-diphenylbutenyne and the unstable 1,3-diphenylbutenyne which reacts further to form oligomeric products.

STRAUS coupling,[1] the non-oxidative head-to-head coupling of terminal alkynes, produces both Z and E isomers of the corresponding enynes (1).[2] Although copper acetylides have been used, only catalytic amounts of cuprous ion are required for the reaction which is normally carried out in acetic acid under nitrogen.[3]

$$RCH{=}CH{-}C{\equiv}CR \qquad\qquad R{-}\overset{\overset{\displaystyle CH_2}{\|}}{C}{-}C{\equiv}CR$$

$$(1) \qquad\qquad\qquad (2)$$

Similar head-to-head couplings, with yields of up to 77% of the E-enyne were observed when terminal alkynes carrying a 3-hydroxy group were heated in benzene in the presence of [RhCl(PPh₃)₃] but no evidence for dimerisation could be obtained with terminal alkynes which did not carry the 3-hydroxy-group. The rhodium complex has also been reported to convert phenylacetylene into the straight chain enyne, E-1,4-diphenylbutenyne, and considerable quantities of oligomeric material. The possible role of the rhodium complex in the formation of the dimeric products has been discussed and brief consideration given to its role in the formation of the oligomers of phenylacetylene.[4,5] Here we report studies which show that terminal alkynes which do not carry a hydroxy-group at C-3 can be catalytically dimerised by the complex to give the branched chain enynes (2; R = alkyl) in high yields. We also provide evidence for the formation from phenylacetylene of the hitherto unreported 1,3-diphenylbutenyne (2; R = Ph) by this method and its spontaneous conversion into oligomers of phenylacetylene.

Whilst studying the role of [RhCl(PPh₃)₃] as a catalyst for the co-oxygenation of unsaturated hydrocarbons,[6] it was noticed that oxygen-free solutions of oct-1-yne in dry benzene reacted slowly at room temperature in the presence of the complex to give two products. For synthetic purposes, a suspension of the complex was stirred with neat oct-1-yne at room temperature under an atmosphere of nitrogen. The product formation was monitored by g.l.c. and the pure products, isolated by preparative g.l.c., were identified as E-hexadec-7-en-9-yne (1; R = C₆H₁₃) and 7-methylenepentadec-8-

yne (2; R = C₆H₁₃) on the basis of their analyses, spectroscopic properties (see Experimental section), and their catalytic reductions to hexadecane and 7-methylpentadecane respectively. A slow loss of catalytic activity accompanied the dimerisation and some unchanged monomer was recovered. The major product, the branched chain isomer (2; R = C₆H₁₃), was obtained in an 87% yield based on total dimer. Hept-1-yne and hex-1-yne reacted in an analogous manner and gave only marginally lower percentages of the branched chain isomers.

The behaviour of phenylacetylene in the presence of the rhodium complex was examined in a similar manner. The g.l.c. trace showed the initial appearance of two volatile products in approximately equal quantities. The product with the longer retention time was subsequently isolated and characterised as the E-1,4-diphenylbutenyne (1; R = Ph) which has been previously obtained in this manner.[4,5] After the reaction had progressed for a few hours the concentration of the second product became constant in contrast to that of the 1,4-diphenylbutenyne which grew steadily until the reaction mixture had become semisolid. G.l.c.–mass spectrometry showed a strong molecular ion, m/e 204, for the second component which was, therefore, isomeric with E-1,4-diphenylbutenyne. Small samples of this material, obtained by preparative g.l.c., were found to decompose steadily to involatile products during a period of 6 h in benzene at similar concentrations to those in the reaction flask. However the isomer was stable enough, in deuteriochloroform at -40 °C, to enable an n.m.r. spectrum to be obtained. This showed, in addition to aromatic protons, two coupled olefinic protons at δ 6.30 and 6.54 ($J = 0.8$ Hz). The low coupling constant and the chemical shifts indicate gem vinylic protons and the spectroscopic findings are consistent with the unstable compound being 1,3-diphenylbutenyne.

The Straus dimerisation of oct-1-yne was re-examined and the $Z:E$ isomer ratio (43 : 57)[3] confirmed for the hexadecenynes produced. No evidence for $Z \longrightarrow E$ isomerism was obtained and the amount of methylenepentadecyne formed under these conditions was less than 1%. Z-Hexadecenyne, isolated from this reaction,

[1] F. Straus, *Annalen*, 1905, **342**, 190.

[2] M. Akhtar and B. C. L. Weedon, *Proc. Chem. Soc.*, 1958, 303; M. Akhtar, T. A. Richards, and B. C. L. Weedon, *J. Chem. Soc.*, 1959, 933.

[3] E. V. Dehmlow, *Z. Naturforsch (B)*, 1966, 815.

[4] H. Singer and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 849.

[5] R. J. Kern, *Chem. Comm.*, 1968, 706.

[6] G. Read and P. C. Walker, *J.C.S. Dalton*, 1977, 883.

was stirred with RhCl(PPh$_3$)$_3$ in degassed benzene at room temperature for 6 h. No conversion into the E-isomer could be detected and it is concluded that the Z-compound is not the precursor to E-hexadecenyne formed in the rhodium-catalysed reaction.

Our findings demonstrate that a 3-hydroxy-group is not essential for dimerisation of terminal alkynes with RhCl(PPh$_3$)$_3$. However the 3-hydroxyalkynes appear to dimerise much more rapidly than the unsubstituted terminal alkynes under the conditions employed by Wilkinson,[4] presumably because of their stronger co-ordinating properties. The marked stereoselectivity observed in the case of the unsubstituted alkynes suggests that the steric requirements of the aliphatic residues are exerting some control on the nature of the intermediates. The early formation of a complex such as (3), in which the saturated chains lie on opposite sides

(3)
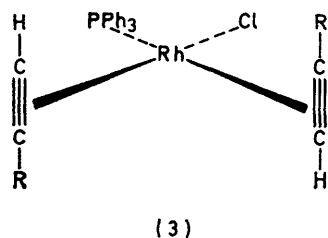
of a square planar complex rather than on the same side, would result in a suitable disposition for subsequent C-1 to C-2 coupling.

It is well known that butenyne and its simple homologues spontaneously polymerise at room temperature and the observed instability of 1,3-diphenylbutenyne is not surprising. We have no reason to suppose that the rhodium catalyst plays any part in the further transformations of this product and it appears probable that RhCl(PPh$_3$)$_3$ is a specific catalyst for the dimerisation of terminal acetylenes. A brief note by Hagihara[7] reports the formation of dimers of type (2) at a catalyst derived from chromium tetrabutoxide and diethylzinc (3 : 1) but with this exception the reaction described here contrasts sharply with reactions of other transition-metal complexes, e.g. [Ni(CO)$_3$(PPh$_3$)],[8] and Ziegler–Natta type catalysts, e.g. TiCl$_3$·Et$_3$Al,[9] which give complex mixtures of oligomeric and polymeric products with terminal alkynes.

EXPERIMENTAL

A Perkin-Elmer 357 spectrophotometer and a Unicam SP 1800 spectrophotometer were used to record, respectively, the i.r. and u.v. spectra. ^{1}H N.m.r. spectra of samples in deuteriochloroform at 25 °C (except where indicated), were recorded using either a JEOL JNM-MH-100 instrument or a JEOL JNM-PS-100 instrument. Mass spectra were determined using a V.G. Micromass 16F mass spectrometer.

For analytical g.l.c. a Pye GCD gas chromatograph was used with (i) a 9 ft 10% PEG A column and (ii) a 5 ft 3% OV17 column. Preparative g.l.c. was carried out with a Pye series 105 instrument using a 6 ft 2.5% SE30 on Chromasorb C-AW column and as a standard procedure fractions obtained were further distilled using a Büchi GKR-50 still.

Acetylenic substrates (purity >98%) were obtained from Koch–Light Laboratories and were used without further treatment. Chlorotris(triphenylphosphine)rhodium was prepared by the method described by Wilkinson.[10] Elemental analyses were carried out by the Butterworth Laboratories.

Oct-1-yne Dimerisation with [RhCl(PPh$_3$)$_3$].—Nitrogen was bubbled through the alkyne (2.5 cm^3) in a conical flask (5 cm^3) for 5 min before the [RhCl(PPh$_3$)$_3$] (0.04 g) was added and the flask closed by a Subaseal cap. The mixture was stirred with a magnetic stirrer for 24 h. Samples taken at intervals during this period and analysed by g.l.c. showed only starting material and two other components. Preparative g.l.c. (160 °C) on a portion of the products (1.8 cm^3) gave, in addition to oct-1-yne (0.5 g), *7-methylene-pentadec-8-yne* (2; R = C$_6$H$_{13}$) (0.48 g) as an oil, n_D^{25} 1.460 0 (Found: C, 87.0; H, 12.8. C$_{16}$H$_{28}$ requires C, 87.2; H, 12.8%), M^+ 220, $\nu_{max.}$ (film) 3 090 (-CH=), 2 230 (-C≡C-), and 1 612 and 894 cm^{-1} (C=CH$_2$); $\lambda_{max.}$ (EtOH) 224 and 233 nm ($\varepsilon_{max.}$ 11 500 and 10 000 respectively), δ_H 5.11 (1 H, d, J 2.2 Hz, vinylic H), 5.20 (1 H, d, J 2.2 Hz, vinylic H), and (E)-*hexadec-7-en-9-yne* (1; R = C$_6$H$_{13}$) (0.05 g) as an oil, n_D^{25} 1.469 0 (Found: C, 87.2; H, 12.8. C$_{16}$H$_{28}$ requires C, 87.2; H, 12.8%), M^+ 220, $\nu_{max.}$ (film) 3 020 (-CH=), 2 220 (-C≡C-), and 955 cm^{-1} (-CH=CH-,E); $\lambda_{max.}$ (EtOH) 226 nm ($\varepsilon_{max.}$ 25 500), δ_H 5.44 (1 H, dt, J 15.6 and 1.7 Hz, H-8) and 6.05 (1 H, dt, J 15.6 and 6.9 Hz, H-7).

Purified samples of both dimers were reduced in ethanol over a 5% Pd–C catalyst with hydrogen at atmospheric pressure and room temperature for 1 h. When compared by g.l.c. the product obtained from isomer (2; R = C$_6$H$_{13}$) was indistinguishable from an authentic sample of 7-methylpentadecane prepared by classical methods from 1-bromo-octane and octan-2-one. The g.l.c. characteristics of the product obtained from the E-isomer (1; R = C$_6$H$_{13}$) was indistinguishable from an authentic sample of hexadecane.

Straus Coupling of Oct-1-yne.—A solution of cuprous acetate was prepared by heating cuprous oxide (0.8 g) in acetic acid (30 cm^3) under a nitrogen atmosphere. Oct-1-yne (6 g) was added and the solution stirred under nitrogen at 70 °C for 24 h. After work-up the components in a portion (0.8 cm^3) of the crude products (4.5 g) were separated by preparative g.l.c. at 175 °C. In addition to unchanged oct-1-yne, three products were isolated. These were identified as (Z)-hexadeca-7-en-9-yne (0.08 g), a colourless oil, n_D^{25} 1.467 0, $\nu_{max.}$ (film) 3 022 (-CH=) and 2 220 cm^{-1} (-C≡C-); $\lambda_{max.}$ (EtOH) 226.5 nm ($\varepsilon_{max.}$ 17 700); δ_H 5.40 (1 H, d, J 11.2 Hz, H-8) and 5.77 (1 H, dt, J 11.2 and 7.2 Hz, H-7), (E)-hexadec-7-en-9-yne (0.112 g), and hexadeca-7,9-diyne (0.034 g).

The last two compounds were indistinguishable from, respectively, the linear enyne prepared in the preceding

[7] N. Hagihara, M. Tamura, H. Yamazaki, and M. Fujwara, *Bull. Chem. Soc. Japan*, 1961, **34**, 892.
[8] L. S. Meriwether, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, 1961, **25**, 5163.

[9] G. Natta, P. Pino, and G. Mazzanti, Italian Pat., 530,753/ 1955.
[10] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

dimerisation and authentic diyne prepared from oct-1-yne by Eglington coupling,[11] in terms of retention times on columns (i) and (ii), i.r. spectra, and n.m.r. spectra.

[11] G. Eglington and A. R. Galbraith, *Chem. and Ind.*, 1956, 737.