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COORDINATION SYNTHESIS ON METAL CENTERS
IV* REACTION OF n-BUTYL- AND *p*-TOLYLCHROMIUM SYSTEMS WITH ACETYLENES

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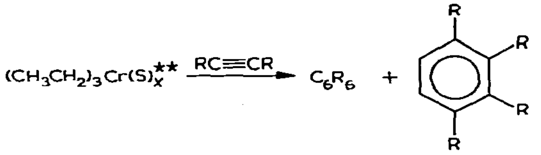
SUMMARY

The interaction of the n-butylchromium system with 2-butyne, in the presence and absence of 1-decene, and with 4-octyne has been studied. The acetylene and olefin compete in their reaction with the alkylchromium system; either the acetylene is oligomerized or the olefin is isomerized. No evidence for acetylene isomerization was found.

Tris-*p*-tolylchromium reacts with 2-butyne to give exclusively 1,2,3,4,6-pentamethylnaphthalene and hexamethylbenzene.

INTRODUCTION

The ethylchromium system reacts with certain disubstituted acetylenes to give, amongst other products, the hexasubstituted benzenes (trimerization of the acetylene) or the tetrasubstituted benzene (from two acetylenes and one of the alkyl groups bonded to chromium) eqn. (1)[1]. The methyl chromium system has recently been shown to promote not only these two types of processes but also the methylation and reduction of the acetylene[2,3] [eqn. (2), R = Ph].



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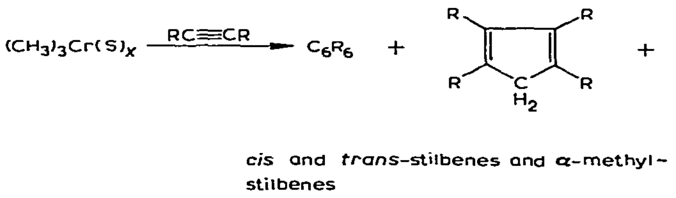

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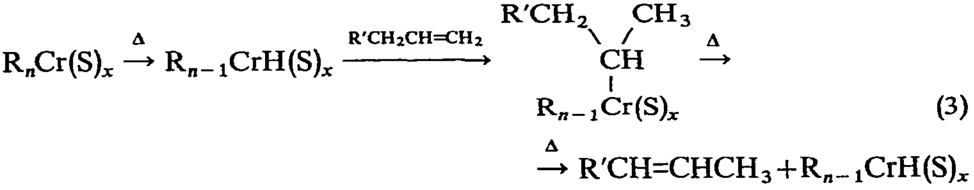
* For Part III see ref. 9.

** Throughout the text $(S)_x$ represents tetrahydrofuran of solvation.

In both cases one of the key steps involves the transfer of an alkyl group originally bonded to chromium to the acetylenic substrate.

Alkylchromium systems are also known to promote the isomerization of terminal olefins, a reaction which proceeds via the formation and fragmentation of a secondary alkylchromium compound[4,5] [eqn. (3)]. It therefore seemed possible that the higher alkylchromium systems might promote the isomerization of acetylenes



$$R_nCr(S)_x \xrightarrow{\Delta} R_{n-1}CrH(S)_x \xrightarrow{R'CH_2CH{=}CH_2} \begin{array}{c} R'CH_2\quad CH_3 \\ \diagdown\ / \\ CH \\ | \\ R_{n-1}Cr(S)_x \end{array} \xrightarrow{\Delta} \tag{3}$$

$$\xrightarrow{\Delta} R'CH{=}CHCH_3 + R_{n-1}CrH(S)_x$$

and/or the cooligomerization of terminal olefins and acetylenes. The interaction of the tri-n-butylchromium system with 2-butyne (in the presence and absence of 1-decene) and with 4-octyne was therefore studied. The system tri-*p*-tolylchromium/ 2-butyne was used as comparison standard.

RESULTS AND DISCUSSION

Tri-n-butylchromium system with disubstituted acetylenes

(*a*). *With 4-octyne.* The final hydrolysis products from the interaction of the tri-n-butylchromium system with 4-octyne at −70 to +20° consisted of a complex mixture of hydrocarbons. The volatile material consisted mainly of unreacted 4-octyne, no other isomeric octynes were present. The less volatile material consisted of at least six compounds the major one of which was crystalline hexa-n-propylbenzene.

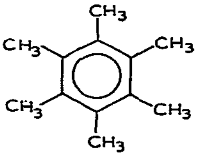
(*b*). *With 2-butyne, in the presence and absence of added 1-decene.* Initial experiments (see Experimental, Table 1, expts. 1–3) established that 2-butyne is oligomerized by the tri-n-butylchromium system to a complex mixture of hydrocarbons. The latter consisted of hexamethylbenzene (20%, based on butyne), other oily aliphatic and aromatic hydrocarbons and polymeric materials. The trimerization of the acetylene takes place in the temperature range −40° to 20°. Further heating of the reaction mixture has little effect on the final yield of hexamethylbenzene.

When the same reaction is carried out in the presence of terminal olefin (1-decene) the final products depend critically upon the order, and temperature, of addition of the reagents. There are three main types of products: (*i*) an octene (see Experimental) formed perhaps by coupling of a butyl group and 2-butyne?; (*ii*) isomerization products of the added 1-decene; and (*iii*) oligomerization products of the acetylene. The results, summarized in Table 1, B, show that when the 2-butyne is added at low temperatures, the 1-decene is not isomerized and the products involve reaction with the acetylene. On the other hand, if the alkylchromium system is allowed to warm, in the presence of 1-decene to 20° *prior* to the addition of the acetylene, then the products consist mainly of isomeric decenes. It is evident, from these brief experiments, that when the acetylene is oligomerized the olefin is not isomerized, and conversely when the olefin is isomerized the acetylene is not oligomerized. This would imply that different catalytic systems are involved in the isomerization of olefins and in the trimerization (oligomerization) of acetylenes. In the initial stages, it is evident that the acetylene competes, to the exclusion of the alkene, in reaction with the trialkylchromium system.

There was no evidence, in the above work, for the formation of products which could arise by the isomerization of the acetylene or by the co-oligomerization of added olefin (1-decene) and acetylene.

Tri-p-tolylchromium with 2-butyne

The interaction of tri-*p*-tolylchromium[6] with 2-butyne leads to good yields of two main products, together with traces of several other hydrocarbons. The former, which account for the major part of the 2-butyne consumed were identified as hexamethylbenzene (I) and 1,2,3,4,6-pentamethylnaphthalene (II)[7] (see Experimental). There was no evidence for the formation of the isomeric 1,2,3,4,5-pentamethylnaphthalene (III).



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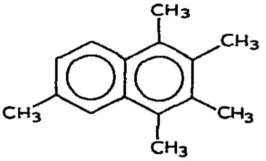

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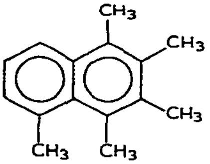
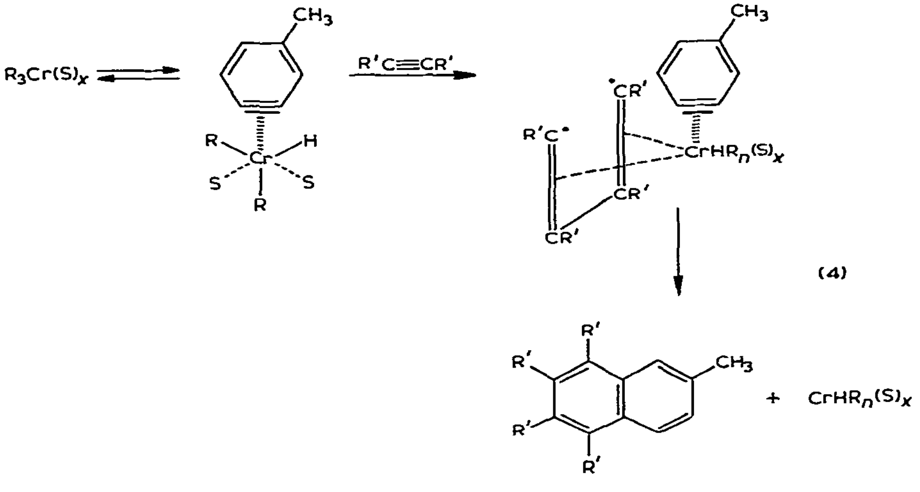


(III)

These results show that in the interaction of σ-bonded arylchromium compounds, like that of the homologous α-naphthylchromium compounds[1], with disubstituted acetylenes it is the carbon bonded to the metal which is involved in the formation of the cyclization products.

The high yields and specificity of products observed in the reaction of the present and other[1] arylchromium compounds contrast sharply with moderate yields and complexity of products associated with the reactions of the alkylchromium systems[1-3]. This difference can be related to the various hydrogen transfer processes associated with the chromium center[1-6,8,9]. Thus the present results with the *p*-tolylchromium system strongly favours the "benzyne mechanism" over the alternative



(4)

"radical mechanism" for the formation of the pentamethylnaphthalene. In this, it was suggested that the aryne complex interacts with two molecules of acetylene[8], complexed to the metal either as a cyclobutadiene or a butadiene diradical[9] [eqn. (4), $R = CH_3C_6H_4$–]. Recent evidence[10] with specifically deuterated 2-butyne apparently rules out the cyclobutadiene complex, leaving the butadiene diradical[11] as the probable intermediate.

Alkylchromium compounds on the other hand can undergo at least four fragmentation processes[5] thereby giving rise to a variety of active intermediates, and hence to a variety of products[2,3].

EXPERIMENTAL
(with Miss U. Feisst)

The general techniques employed in the preparation and handling of air and moisture sensitive organometallic compounds have already been described[9]. Gas chromatographic (GC) analysis were carried out on an F & M model 5750, equipped with a 12 ft, 20% Carbowax 20M column (for the separation of 4-, 3-, 2-, and 1-octynes and the decenes) and a 4 ft, 10% Silicone Gum Rubber for the higher boiling aromatic compounds. Column chromatography was carried out on alumina columns, using hexane, benzene, chloroform and methanol as eluting solvents.

Microanalyses were by Mr. A. Peisker, Brugg, Switzerland and Mr. W. Manser of the Eidg. Technische Hochschule, Zürich, Switzerland.

Tri-n-butylchromium system with 4-octyne

4-Octyne (10 ml) was added to a suspension of the tri-n-butylchromium system [from alkyl-Grignard (40 ml, 31.5 mmoles) and $CrCl_3 \cdot 3THF$ (3.9 g, 10.4 mmoles)] in tetrahydrofuran (50 ml) at −30°. The whole was allowed to warm to 20°, and after 14 h was heated under reflux (2 h). The cooled reaction mixture was hydrolyzed and the organic material isolated with the aid of ether. The volatile products (b.p. up to 170°/15 mm) were separated by distillation and shown (GC analysis) to consist of unreacted 4-octyne [δ_{TMS} 1.00 (multiplet, 6 protons, CH_3); 1.46 (multiplet, 4 protons, CH_2); 2.1 (multiplet, 4 protons, $CH_2C\equiv$)] and traces of substances with the same retention times as *cis*- and *trans*-4-octenes. The distillation residue was shown by GC analysis (Silicone column) to contain at least six compounds. Column chromatography (activated alumina) effected the separation of the major constituent. It was obtained as white needles m.p. 99–102° (Ex. EtOH). (Found: C 87.3, H 12.7. $C_{24}H_{42}$ calcd.: C 87.2; H 12.8%.) δ_{TMS} 1.0 (multiplet, 3 protons CH_3); 1.5 (multiplet, 2 protons CH_2); 2.4 (multiplet, 2 protons $ArCH_2$). The above data are in accord with the substance being hexa-n-propyl benzene (lit.[12] m.p. 103°).

Tri-n-butylchromium 2-butyne, in absence and presence of 1-decene

(*a*). *In the absence of 1-decene.* Solutions of the tri-n-butylchromium compound [from alkyl-Grignard (40 ml, 31.5 mmoles) and $CrCl_3 \cdot 3THF$ (3.9 g, 10.4 mmoles)] in tetrahydrofuran (50 ml) were treated, at −40°, with 2-butyne (10 ml). In the individual experiments the reaction mixtures were warmed to (1) 0° for 96 h; (2) +20° for 19 h; (3) +20° for 14 h and heated under reflux [CO_2/acetone condenser] 2 h. In each case the final reaction mixtures were hydrolyzed at +20° and the organic material isolated with the aid of ether. The ether was removed by distillation from the crude extracts and the residues (1.89 g, 2.00 g, 2.70 g respectively) chromatographed on neutral alumina (activity 1). The materials isolated in this way (Table 1, expts. 1–3) consisted of (1) air sensitive oils whose ^{1}H NMR spectra showed complex adsorption in the δ_{TMS} 0.5 to 2 region; (2) hexamethylbenzene, m.p. and mixed m.p. 160–161°, δ_{TMS} 2.13 (singlet); (3) red viscous materials.

TABLE 1

PRODUCTS FROM n-BUTYLCHROMIUM SYSTEM WITH 2-BUTYNE IN THE ABSENCE (A) AND IN THE PRESENCE (B) OF 1-DECENE

Exp. No.	Temp.[a]	Temp.[b]	Products						
			Alkane[c]	1-Alkene[c]	*trans*-2-Alkene[c]	*cis*-2-Alkene[c]	Oils[d]	HMB[d,e]	Polymers
A									
1		0					0.4	0.9	+
2		20					0.5	1.1	+
3		20–60					0.5	1.3	+
B									
4	−30	20/60	2.0	98.0	0.0	0.0	0.6	1.3	+
5	+10	20/60	4.9	92.4	1.8	0.8	+	0.7	+
6	20	60	10.7	20.7	47.6	20.9	[f]	[f]	[f]

[a] Temperature in °C, at which the 2-butyne was added. [b] Final temperature in °C of total reaction mixture. [c] Relative percentages in total alkane/alkene fraction. [d] Weight in g. [e] Hexamethylbenzene (HMB). [f] Traces of material.

(*b*). *In the presence of* 1-*decene*. In an analogous set of experiments the n-butylchromium system [from n-alkyl-Grignard (40 ml, 31.5 mmoles) and $CrCl_3 \cdot 3THF$ (3.9 g, 10.4 mmoles)] was allowed to react with 1-decene (10 ml) and 2-butyne (10 ml) under the following conditions.

Table 1, *expt*. 4. Both the alkene and acetylene were added at −30°, the whole allowed to warm to +20° (14 h), and finally refluxed (2 h).

Table 1, *expt*. 5. Alkene added at −30°, reaction mixture allowed to warm to +10° ($\frac{1}{2}$ h) and the acetylene added. The total reaction mixture was allowed to stand at +20° (14 h) and finally refluxed (2 h).

Table 1, *expt*. 6. Alkene added at −30°, reaction mixture allowed to warm to +20° (14 h) alkyne added and total reaction mixture heated under reflux (3 h).

In each case the total reaction mixtures were hydrolyzed at +20°, and the organic material isolated with the aid of ether. The total *alkane/alkenes* were isolated by fractional distillation (and analyzed by gas-chromatography), and the *residues* were chromatographed on alumina (activity 1). The materials isolated in this way (Table 1, Expts. 4–6) consisted of:

Expt. 5. Substances with the same gas chromatographic retention times as 1-octene (traces), decane and 1-decene (the latter was isolated and identified by ^{1}H NMR and IR spectroscopies); air sensitive oils [see under (*a*) above]; hexamethylbenzene m.p. and mixed m.p. 160–161° and red viscous polymers.

Expt. 6. Substances with the same gas chromatographic retention times as 1-octene (traces), decane, 1-decene, *trans*-2-decene and *cis*-2-decene (the 1-decene was isolated and identified as above); the same mixture of oils, crystalline hexamethylbenzene and polymers as above.

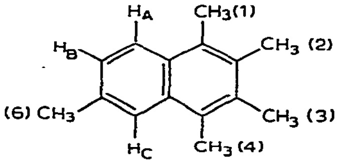
Expt. 7. Substances with the same gas chromatographic retention times as decane, 1-decene, *trans*- and *cis*-2-decene (the last three were isolated and identified by ^{1}H NMR and IR spectroscopies); only traces of residue.

Tri-p-tolylchromium with 2-butyne

2-Butyne (10 ml, 127 mmoles) was added to a suspension of solvated tri-*p*-tolylchromium[6] [from *p*-tolylmagnesium bromide (100 ml, 52 mmoles) and $CrCl_3 \cdot 3THF$ (6.5 g, 17.3 mmoles)] in tetrahydrofuran (50 ml), −70°. The reaction mixture was allowed to warm to 20°, and after standing at this temperature (144 h) was hydrolyzed. The organic material isolated with the aid of ether consisted of a red viscous oil (7.3 g). This was chromatographed on alumina; the hexane eluate (5.4 g) was rechromatographed to give two crystalline products (A) (1.4 g) and (B) (1.95 g) plus oily material (2.0 g). The latter was shown by gas chromatographic analysis to consist mainly of compound A and B together with small quantities of many other hydrocarbons.

Compound A was identified as hexamethylbenzene; m.p. and mixed m.p. 160–161°.

Compound B; m.p. 85–86° (ex. CH_3OH). (Found: C, 90.2; H, 9.6. $C_{15}H_{18}$ calcd.: C, 90.8; H, 9.1%.) Picrate m.p. 175–177° (decompn.). (Found: C, 58.4; H, 5.1; N, 9.1; $C_{21}H_{21}N_3O_7$ calcd.: C, 59.0; H, 4.9; N, 9.8%.) δ_{TMS} for hydrocarbon (numbering is as shown below), 2.24 (singlet, 6 protons, CH_3, 1 and 4); 2.45 (singlet, 9 protons, CH_3 2, 3 and 6); 7.05 (4 lines, 1 proton, H_B, J_{AB} 9 Hz, J_{BC} 2 Hz); 7.6 (multiplet, H_C); 7.725 (doublet, 1 proton H_A, J_{AB} 9 Hz). Decoupling with CH_3 at $\delta = 2.45$ (CH_3 at C_6, C_2 and C_3) gives $\delta = 7.05$ (1 proton, H_B, 4 lines made up of doublet, J_{AB} 9 Hz, *ortho* coupling H_BH_A; and a doublet J_{BC} 2 Hz, *meta* coupling H_BH_C); $\delta = 7.6$ (1 proton, H_C, doublet, J_{BC} 2 Hz, *meta* coupling H_CH_B); $\delta = 7.725$ (1 proton, H_A, doublet, J_{AB} 9 Hz, *ortho* coupling H_AH_B). From this data the crystalline compound B is 1,2,3,4,6-pentamethylnaphthalene (lit. m.p. 85°; picrate m.p. 176°).



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