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COORDINATION SYNTHESIS ON METAL CENTERS
V*. REACTION OF TRIALLYLCHROMIUM(III) AND TETRAALLYLDICHROMIUM(II) WITH 2-BUTYNE

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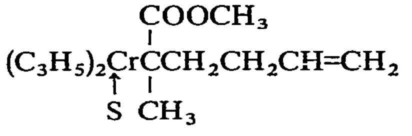
SUMMARY

Both triallylchromium(III) and tetraallyldichromium(II) react with 2-butyne, in tetrahydrofuran solution to give the same overall mixture of products. Three of the four major components have been isolated and identified as 1,2,3,4-tetramethylbenzene, pentamethylbenzene and hexamethylbenzene. The presence of 1,2,3,5-tetramethylbenzene as a minor constituent is implied from gas-chromatographic analysis.

INTRODUCTION

The catalytic activity of triallylchromium(III), and derivatives thereof, in the polymerization of olefin and diene substrates has been described and discussed[2-5]. From the results however it is not always clear whether or not one or more of the allyl groups originally bonded to chromium is (are) involved in product formation. Experiments with labelled triallylchromium[3,4] established that in the reaction with methyl methacrylate one of the allyl groups is transferred to a monomer unit, it was also suggested that the active intermediate in this polymerization is the organochrominium(III) species (I) (S = methyl methacrylate).



$$(C_3H_5)_2\underset{\overset{\uparrow}{S}}{Cr}\underset{CH_3}{\overset{COOCH_3}{C}}CH_2CH_2CH{=}CH_2$$

(I)

In contrast, there is very little known about the reactions of the diamagnetic tetraallyldichromium(II). One report[4] states that it is inactive as an initiator for the polymerization of methyl methacrylate; and another states[6] that it is a potential component in a catalyst for the polymerization of olefins.

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* For Part IV see ref. 1.

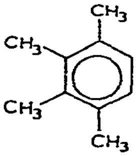
In order to gain preliminary information regarding the relative reactivity of the allyl–chromium(III) and –chromium(II) species, their reaction with 2-butyne has been studied. This reaction was chosen since it not only reflects the catalytic activity of the chromium species (trimerization and polymerization reactions) but also provides information concerning the fate of the organic groups originally bonded to chromium[7].

RESULTS AND DISCUSSION

Triallylchromium(III) and tetraallyldichromium(II) can both be prepared by the interaction of the appropriate stoichiometric ratios of allylmagnesium halide and $CrCl_3(THF)_3$ or $CrCl_2$ [or $CrBr_2(THF)_2$] in tetrahydrofuran[8–10]. The tetraallyldichromium(II) may also be prepared by the thermal[8] or photochemical[10] fragmentation of triallylchromium(III), eqn. (1).

$$(C_3H_5)_3Cr \xrightarrow[\text{or } h\nu]{\Delta} [(C_3H_5)_2Cr]_2 + \text{1,5-hexadiene} \qquad (1)$$

In the present work the allyl-Grignard synthesis was used, and the subsequent reaction of solutions of the allyl–chromium species with 2-butyne were carried out under identical conditions. In both cases the same overall mixture of products was obtained and in both cases these contained the same four major products. Three* of these have been isolated and identified as 1,2,3,4-tetramethyl-, pentamethyl- and hexamethylbenzene(II)–(IV). The possible presence of 1,2,3,5-tetramethylbenzene (V) as a minor product was suggested by coinjection (GLC) with an authentic specimen.



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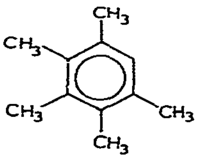

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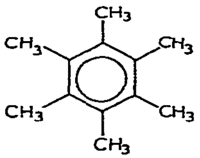

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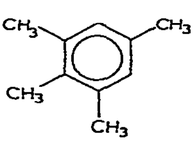

(V)

The major difference in the products from the reaction of the tri- and diallylchromium systems lies in the relative proportion of trimerization product (IV) and of products involving allyl groups [(II), (III) and (V), etc.]. Thus in the case of the allylchromium(II) system the relative amount of hexamethylbenzene was 74% whereas with the triallylchromium(III) it was 60% (see Experimental).

The present reactions resemble those involving other σ-bonded organochromium compounds insofar as the products correspond to those formed by the oligomerization of the acetylene [*e.g.* (IV)] and those formed from two acetylene units and one of the organic groups originally bonded to chromium[11,12] [*e.g.* (III)]. They differ from these however, insofar as a product involving *one acetylenic unit* and two *allyl groups* is also formed**. It will be further noted that in the overall reaction the allyl

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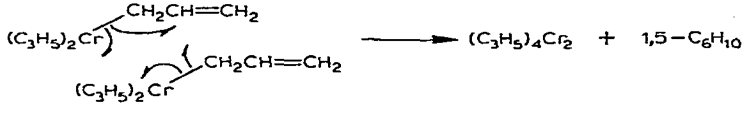
* It has not been possible to isolate sufficient of the fourth compound (by preparative scale GLC) to permit its unambiguous characterization.

** Compounds of this type have recently been detected amongst the products from the reaction of the methylchromium system with diphenylacetylene[12].

groups oroginally bonded to chromium turn up as $CH_3C{=}CH$ units in product, *i.e.* both hydrogen migration and abstraction have occurred.

The interpretation of the reactions of allylchromium compounds, in particular those involving the incorporation of one or more allyl groups in the products, is complicated by the fact that there are, in principle, two possible reaction sites in an allyl group bonded to a metal center. Thus all the reactions known to date involving allylchromium compounds[3–5,8–10] can be interpreted either in terms of reaction at the CH_2 carbon or at the C=C. This is illustrated in formation of 1,5-hexadiene by the thermal or photolytic decomposition of triallylchromium(III)[8–10]. In principle this reaction can involve the head-to-head coupling of two allyl groups via a 4-center transition state [eqn. (2)], or attack on the C=C, *via* the 6-center transition state [eqn. (3) (head-to-tail)], or eqn. (4) (tail-to-tail coupling).



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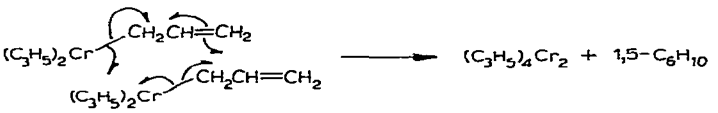

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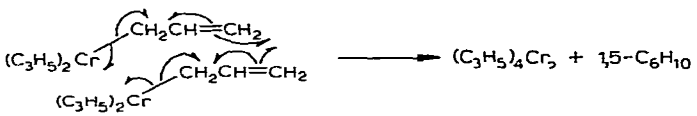
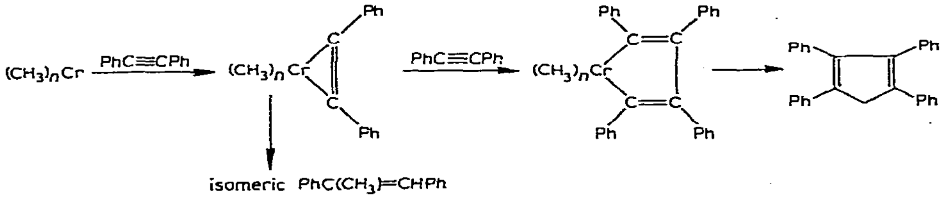


(4)

Various mechanisms have been proposed for the reaction between organochromium compounds and acetylenes. These include, (*i*) the interaction of a butadiene diradical with a benzyne or carbene species within the confines of an organochromium complex[11]; (*ii*) intramolecular rearrangement within an organochromium heterocycle, eqn. (5)[13,14], (*iii*) the stepwise transfer of an organic group bonded to chromium to complexed acetylene[15,16]. Evidence in favour of the latter process was obtained not only from the reactions of the methyl–[15] and deuteromethyl–chromium systems (with tolane) but also from the mesityl–chromium system and 2-butyne[17]*.

In the present work, the formation of pentamethylbenzene can be rationalized



(5)

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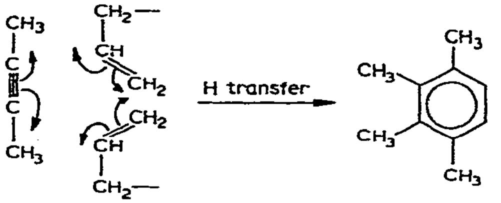
* Support for such a stepwise transfer [(*iii*) above] has recently been obtained in deuterolytic studies of the triphenyl- and trimesitylchromium/2-butyne systems[18].

in terms of any of the above mechanism [(*i*)–(*iii*)]. The formation of 1,2,3,4-tetramethylbenzene [formally from one acetylene and two allyl groups, eqn. (6)] together with only traces of the isomeric tetramethylbenzenes is difficult to explain in terms of the stepwise mechanisms (*ii*) and (*iii*). One possible explanation would involve the synchronous cyclisation of one acetylene and two allyl groups, initiated by the tail-to-tail coupling of the two allyl groups. Further experiments are in progress in order to clarify this point and in particular to determine at which stage the required hydrogen transfers occur.



(6)

EXPERIMENTAL (WITH MR. P. WIDIN)

All reactions with organometallic compounds were carried out as already described[1]. The analytical and preparative gas-chromatography were effected with an F and M gas-chromatograph (Model 5750) equipped with silicone SE 30 columns, (analytical, 3 ft, 1/4 inch; preparative, 3 ft, 1/2 inch). In the preparative work samples were collected by bubbling the helium effluent through carbon tetrachloride.

Triallylchromium(III) with 2-butyne

A solution of triallylchromium [from allylmagnesium chloride (50 ml, 23.4 mmoles) and $CrCl_3(THF)_3$ (2.93 g, 7.8 mmoles) in tetrahydrofuran (50 ml) at −70 to −30°] in tetrahydrofuran was treated at −40° with dry, oxygen-free 2-butyne (10 ml, 6.88 g). The red homogeneous reaction mixture was allowed to warm to room temperature (6 h). After 72 h at this temperature the black heterogeneous reaction mixture was hydrolized (gas evolution). The crude organic material (4.0 g), isolated with the aid of ether (blue extract), was shown by gas-chromatographic analysis to contain 4 major compounds, A (5.9%), B (23.0%), C (60.1%), D (10.9%), together with 11 other minor components. Co-injection, on a silicone SE 30 column, suggested that of the major components, peaks A, B and C were 1,2,3,4-tetramethylbenzene, pentamethylbenzene and hexamethylbenzene respectively, of the minor components one had the same retention time as 1,2,3,5-tetramethylbenzene, but none had the retention time of mesitylene.

The crude material was chromatographed on alumina to give; with hexane hexamethylbenzene (0.203 g), m.p. and mixed m.p. 161–163° (*ex* MeOH), together with a mixture of oil and crystals (1.253 g); with benzene a yellow oil (0.420 g); with chloroform a viscous yellow oil (1.050 g)· The hexane eluate (1.253 g) was further separated by preparative scale GLC into: peak A, colorless oil, δ 6.72 (singlet, 2 protons), 2.14 and 2.20 ppm (two singlets, 12 protons), the infrared spectrum (0.025 mm film) was superposable with that of authentic 1,2,3,4-tetramethylbenzene; peak B, solid, δ 6.64 (singlet, 0.91 protons), 2.12 and 2.15 ppm (two singlets, 15.0 protons), m.p. and mixed m.p. 50–51° (sublimed), picrate m.p. and mixed m.p. 123–127°, the infrared spectrum (KBr) was identical to that of authentic pentamethylbenzene; peak C, solid, m.p. 160–163° alone or with authentic hexamethylbenzene, δ 2.14 ppm (singlet); peak D, oil which was contaminated with a second substance, it was not possible to accumulate enough pure material by preparative scale GLC to permit its identification.

Allylchromium(II) with 2-butyne

A solution of tetraallyldichromium(II) [from allylmagnesium chloride (45 ml, 28.2 mmoles) and $CrBr_2(THF)_2$[19] (3.5 g, 9.83 mmoles) in tetrahydrofuran at −70 to −30°] in tetrahydrofuran was treated at −40° with 2-butyne (10 ml, 6.89 g). The subsequent experimental details are essentially the same as those given above. The crude material (3.020 g) consisted of the same four major compounds, A (2.9%), B (16.0%), C (74.2%), D (6.9%) together with the same other 11 components (co-injection of the two extracts on silicone SE 30). Column chromatography on alumina gave; hexane eluate (1.024 g); chloroform eluate (1.804 g). Gas-chromatographic separation of the hexane eluate gave the major components A, B, C, D, identified by a direct comparison (IR and when appropriate, m.p.) with the specimens isolated from the foregoing reaction.

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