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CYCLIZATION OF DIPHENYLACETYLENE ON METHYLCHROMIUM σ-COMPLEXES

II*. CYCLIC AND LINEAR CONDENSATIONS

M. MICHMAN** AND H. H. ZEISS
Monsanto Research S.A., Eggbühlstrasse 36, CH-8050 Zürich (Switzerland)

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SUMMARY

The reactions of diphenylacetylene with methylchromium systems lead to the formation of condensation products, of which the following have been isolated and identified: *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene; hexaphenylbenzene; 1,2,3-triphenylnaphthalene: 1-methyl-2,3,4-triphenylnaphthalene: 1,2,3,4-tetraphenyl-1,3-cyclopentadiene and 1,2,4,5-tetraphenylbenzene. It is evident that methyl groups of the chromium complex participate in these cyclic condensations via insertions of methylene (carbene) groups into the ring skeleton. These processes are also accompanied by hydrogen-transfer reactions.

INTRODUCTION

It has recently been reported that two classes of products are formed by the reaction of diphenylacetylene with methylchromium systems[1]. The first group consists of products of additions of methyl groups and hydrogen to the alkyne[2], namely, stilbenes, α-methylstilbenes, α-benzylstyrene and traces of bibenzyl. The second group is comprised of products of condensation, cyclic and linear, involving two and three acetylenic units, and this group is the subject of the present paper.

Trimerizations and dimerizations of alkynes on organometallic catalysts are generally well known[3,4]. A specific case of the generation of hexaphenylbenzene (II) and tetraphenylcyclopentadiene (III) by the reaction of diphenylacetylene with a methylchromium reagent has been reported[5]. In the present study this reaction is shown to involve further interactions of the acetylenic ligands with the organometallic reagent.

RESULTS AND DISCUSSION

The condensation products obtained in this reaction are shown below.

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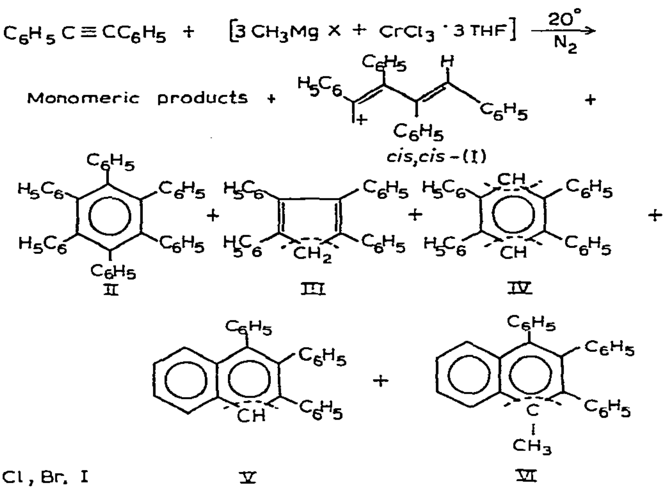
[*] For Part I, see ref. 2.

[**] Present address: Department of Chemistry, The Hebrew University, Jerusalem, Israel.

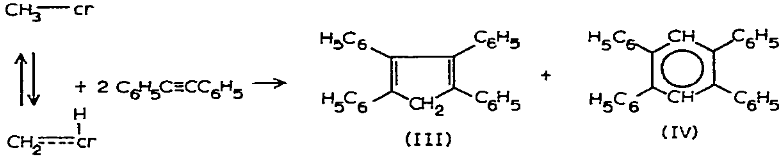


Other possible products, *e.g.* 2,3,8-triphenylbenzofulvene and octaphenylcyclooctatetraene were shown to be absent by gas chromatographic analysis. The former compound has been reported[6] to be formed in the reaction of diphenylacetylene with $(C_6H_5CN)_2PdCl_2$.

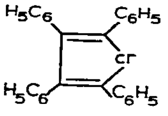
The methylchromium complex, generated from $CrCl_3 \cdot 3THF$ and methylmagnesium halide at −70°, decomposes on warming to room temperature. The addition of diphenylacetylene to solutions of this complex at −40° results presumably in the binding of the alkyne as a ligand at the reaction site. When the molar ratio of alkyne to chromium exceeds 1/3 the excess of acetylene is recovered unchanged: however, below this limit it is fully consumed. In practice, an excess of acetylene is maintained throughout the reaction in order to ensure optimum yields. With a large excess of methylmagnesium halide over chromium salt, *i.e.* a 11/1 molar ratio, compound (VI) becomes a major condensation product.

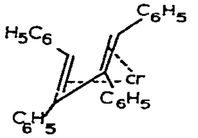
In the usual procedure, a 3/1 molar ratio of Grignard reagent to chromium salt was used[2], and resulted in a mixture of some twelve products. The six described here were isolated and identified with certainty. The remainder were shown to be present in small amounts by gas chromatography. The combined yield of all condensation products generally amounted to a 50–60% yield based on diphenylacetylene consumed. Compounds (II), (IV) and (VI) were obtained in relatively high yield, while (III) was detected only after relatively long reaction times.

The formation of hexaphenylbenzene is obviously the result of the trimerization of diphenylacetylene, but tetraphenylbenzene and tetraphenylcyclopentadiene arise from the condensation of two acetylenic units and methyl or methylene groups with dehydrogenation. The insertion of carbon atoms in these cases bears a formal resemblance to the condensations of acetylenes on carbonyl complexes of transition metals: tetraphenylcyclopentadienone from (diphenylacetylene)iron carbonyl complexes[7], and tetramethylbenzoquinone from 2-butyne and iron pentacarbonyl[8]. In the present work it is not clear whether the carbon atoms are inserted as methyl or methylene (carbene), although an argument can be advanced for the latter[2,9]. There is evidence available[9] indicating that a migration of hydrogen takes place between the methyl group of the methylchromium complex and the chromium center, leading to the generation of a transient carbene–chromium intermediate. Such species juxtaposed to dimerizing diphenylacetylene would lead to products (III) and (IV). The origins of other products from this reaction, α-methylstilbene and α-benzylstyrene[2], can also be rationalied in terms of these intermediates.

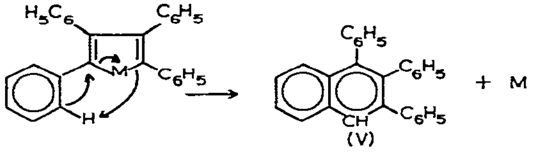


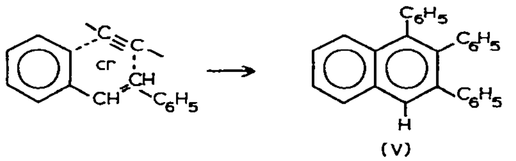
The dimerization of diphenylacetylene, leading eventually to (III), has been interpreted in terms of a five-membered metallocyclic ring system[10]. Alternatively, a butadiene diradical is also a possibility. Neither rationalization can be eliminated nor secured with present data. However, several examples of the former type have been observed[11,12].

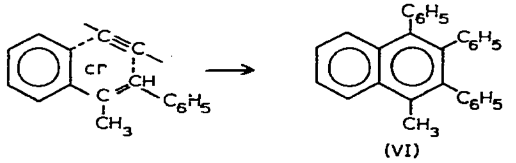




Formation of the naphthalenes (V) and (VI) requires discussion since it is not all compelling to believe that they are primary condensation products. While the origin of (V) may be considered as a cyclic condensation with transfer of *ortho*-hydrogen, this does not apply to the synthesis of (VI). If (V) and (VI) arise by a similar pathway, then it is more accurate to consider these compounds as the products of a common intermediate chromium complex in which either a methyl group or a hydrogen atom is transferred; or as secondary products of a further condensation of diphenylacetylene and the primary linear condensation compounds, stilbene, α-methylstilbene and α-benzylstyrene[2].







It is clear that methylchromium complexes are potent systems for hydrogen and methyl group transfer reactions in the presence of an acceptor. The complicated pattern of linear and cyclic condensations observed requires further examination with respect to the origin and destination of the hydrogen atoms involved in these processes.

EXPERIMENTAL

Reaction conditions and separation of products

The standard procedure[2] is used taking care to have an excess of diphenylacetylene, and after hydrolysis the products are extracted with diethyl ether. The concentrated extract is chromatographed with hexane over non-activated silica. After elution of the monomeric addition products a yellow fraction is obtained which when treated with hexane and ethanol yields crystals of tetraphenylbenzene and tetraphenylbutadiene. This particular fraction may then be repeatedly chromatographed and the rest of the products are obtained when elution is continued with benzene. The eluant composition was checked by VPC using a 1/8″ 6′ 10% UC-W-96 silicon oil on a Chromosorb P column operated at 275°. The various peaks are identified with authentic samples. Collection of material by VPC on a corresponding 1/4″ column is possible but tedious. Special details helpful for isolation are given under individual compounds.

1,2,3,4-*Tetraphenyl*-1,3-*butadiene*

This compound, eluted together with tetraphenylbenzene was identified by VPC, NMR and mass spectrometry. Since separation from the benzene derivative was difficult, single crystals were selected and used for m.p. determination and X-ray examination. The m.p. was 184°, and single crystal diffraction photographs showed it to be identical with authentic *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene[13]. The authentic sample was prepared by the action of lithium on diphenylacetylene under a nitrogen atmosphere[14,15]. After 24 h the solution was filtered and the filtrate hydrolyzed to yield the product which was recrystallized from acetic acid and washed with water.)

1,2,3-*Triphenylnaphthalene*

The authentic sample of this material was also isolated from the reaction of lithium with diphenylacetylene[14], by hydrolyzing the less soluble residues. In this case long reaction times are advantageous. Recrystallization from ethanol or acetic acid yielded the product, m.p. 152°. This compound was not isolated in a satisfactorily pure state from our reaction mixture but was detected by mass spectrometry and identified by VPC and by thin-layer chromatography (TLC). The latter was carried out on Kieselgel G plates using a mixture of benzene and light petroleum (b.p. 40°) in a ratio of 60–40 as a developer. Detection was accomplished by illumination with UV light or by exposure to iodine vapor. With the latter, triphenylnaphthalene gave a pink coloration and not the characteristic brown color shown by most aromatics, making the identification more conclusive.

1-*Methyl*-2,3,4-*triphenylnaphthalene*

In runs carried out with a ratio of 10/3/1 of Grignard reagent to chromium salt to diphenylacetylene, this compound was the major product as indicated by the NMR spectrum and the VPC trace. It was eluted from a column of activated silica by a 10/1 hexane/benzene mixture as a colorless oil which crystallized immediately upon the addition of a drop of hexane. Recrystallization is best carried out from ethanol. The NMR spectrum showed 4 intense bands at τ 7.48, 3.26, 2.95, 2.90, and complex low intensity patterns at 1.9 and 2.5 ppm.; the ratio of area of the first peak to that of all the others combined was 3/19.5. (CCl_4 was used as a solvent and TMS as an internal standard.

A sample for comparison was prepared as follows. To a slurry of 2 g (4 mmole) of 1-iodo-2,3,4-triphenylnaphthalene[16] in 100 ml dry ether, 30 ml of 0.5 *N* methyllithium (a large excess) were added with stirring under argon. A brown color appeared but quickly vanished. Dry benzene (10 ml) was added and the slurry refluxed for 4 h, left at room temperature for another 40 h, and hydrolyzed. The dry organic phase yielded after evaporation a yellow oil which when chromatographed on activated silica with 10/1 hexane/benzene yielded a mixture of methyltriphenylnaphthalene (60%), and triphenylnaphthalene (40%). Total yield was around 90%. The first compound could be isolated by repeated crystallizations from ethanol, m.p. 155°, undepressed by admixture with an authentic sample.

1,2,4,5-*Tetraphenylbenzene*

This compound was isolated in crystalline form from runs in which an excess of diphenylacetylene was maintained throughout. When eluted from silica it was accompanied by 1,2,3,4-tetraphenyl-1,3-butadiene as shown by VPC, NMR and mass spectromety. Recrystallization from hexane yielded needles having m.p. 265°. Very characteristic crystal transitions were observed with a Kofler hot bench microscope at about 190° and 240°. (Found: C, 93.9; H, 6.14. $C_{30}H_{22}$ calcd.: C, 94.2; H 5.76%.) The structure was further established by mass spectroscopy which showed an extremely stable molecular ion. NMR spectrum (in CCl_4), showed two sharp absorptions at τ 2.87 and 2.59 ppm (relative intensity 10/1). The low-field resonance is assigned to the protons of the central ring. An authentic sample was prepared according to Schönberg *et al.*[17]. Later the compound was obtained in improved yield by heating 1,3,4,6-tetraphenyl-3,4-dichloro-1,5-hexadiene at 250° for several minutes under an inert atmosphere.

1,2,3,4-*Tetraphenylcyclopentadiene*

Traces of this compound were detected by the typical NMR absorption at τ 6.06 and by VPC. A sample was prepared according to Ziegler and Schnell[18]. NMR data: two single bands at τ 2.94 and 6.06 ppm (area ratio of 10/1). UV data: λ_{max} 344 mμ (ε 6000).

Hexaphenylbenzene

This compound, the least soluble product, can be isolated directly as a yellow powder from the organic phase after hydrolysis. It is eluted last, preferably by benzene, among the condensation products and often contaminates fractions from chromatography. The compound is recrystallized from dichloro- or dibromomethane. The m.p. is 462° but the compound can easily be recognized by a crystal transition at 280°. It is also soluble in dioxane and less so in benzene. A full X-ray structure analysis has recently been carried out by Dr. Bart of these laboratories[19]. A sample was prepared according to Blomquist and Maitlis[6].

1-Benzylidene-2,3-diphenylindene (*2,3,8-triphenylbenzofulvene*)

This was prepared according to Smith and Hoehn[15].

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