

CYCLIZATION OF DIPHENYLACETYLENE ON METHYLCHROMIUM σ -COMPLEXES

I. HYDROGENATION AND TRANSMETHYLATION

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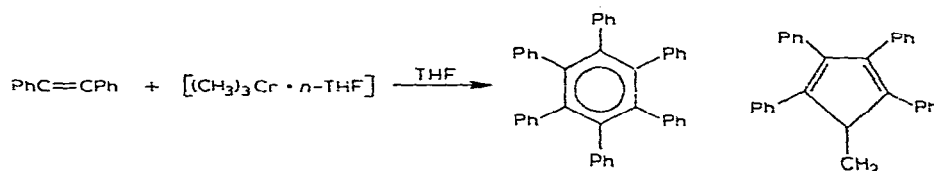
(Received August 10th, 1968)

SUMMARY

The cyclic and linear condensations of diphenylacetylene in the presence of the methylchromium tetrahydrofuranate system are accompanied by reactions with the methyl-metal complex, namely transfer of methyl groups and hydrogen to the unsaturated ligand. *cis*- and *trans*-Stilbenes, α -methylstilbenes, α -benzylstyrene, and dibenzyl are formed among other condensation products. The additions are sterically controlled; the *cis* isomers initially formed isomerize to the *trans* olefins. The abstraction and transfer of hydrogen occur within the system and either the methyl groups or the solvent act as the major sources. Methyl transfers were also observed when methylmagnesium halide and diphenylacetylene were treated with halides of cobalt and nickel. Methylmagnesium chloride alone, methyllithium or trilithium hexamethylchromium failed to react with the alkyne.

INTRODUCTION

In 1959 the observation was made that in the reaction of diphenylacetylene with methylchromium reagents, cyclic condensation took place accompanied by incorporation of a methylene group into a ring system¹ (Fig. 1; Ph = C₆H₅; THF = tetrahydrofuran):



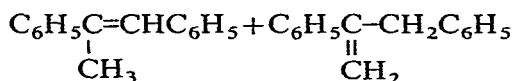
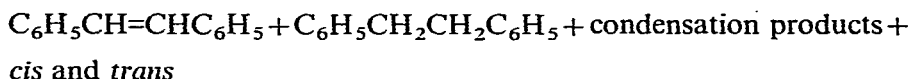
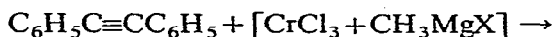
Similarly, with triethylchromium 1,2,3,4-tetraphenylbenzene was obtained, indicating that an ethylidene group was incorporated with concurrent dehydrogenation. The latter action was attributed to chromium since with the diethylnickel compound the equivalent reaction produces a cyclo-1,3-hexadiene derivative.

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We recently found that several other cyclic and linear condensations as well as insertions and additions also occur in this system². Presently, addition reactions are discussed, which do not involve condensations.

RESULTS AND DISCUSSION

Diphenylacetylene was allowed to react with methylchromium reagent freshly prepared by the reaction of methylmagnesium chloride with $\text{CrCl}_3 \cdot 3\text{THF}$ under a nitrogen atmosphere.



cis and trans

The alkyne was fully consumed. Condensation and addition products were formed in approximately the same amounts. The yields within the last group are of the order of 45% stilbenes, 30% methylstilbenes, 20% benzylstyrene and little dibenzyl. These are approximate values after a 30–40 h run. The product ratios change considerably with time.

All products were isolated, except dibenzyl which was identified in impure extracts. Identification was done by m.p. if possible, NMR, VPC, mass spectrometry, IR and TLC. All products were compared with authentic samples. Traces of other products were observed such as $\text{C}_{16}\text{H}_{16}$ which was detected by mass spectrometry. Phenanthrene and 9-methylphenanthrene, which would have been formed as a result of hydrogen abstraction from the phenyl ring, were shown by VPC to be absent in the product mixture. Also, 1,2-diphenylpropane could not be detected among the products.

In order to establish the essential function of the chromium, methylmagnesium chloride was treated with diphenylacetylene under identical conditions. Similar experiments were also carried out with methyllithium. Both experiments were concluded with negative results. The lack of reaction of those reagents with diphenylacetylene under somewhat different conditions is reported already^{3,4}. Remarkably, no hydrogen or methyl transfer were observed when the solid, isolable complex $\text{Li}_3\text{Cr}(\text{CH}_3)_6$ dioxanate⁵ was allowed to react with diphenylacetylene. On the other hand, qualitative results indicating the formation of hydrogen and methyl transfer products, were obtained when $\text{CrCl}_3 \cdot 3\text{THF}$ was substituted by anhydrous CoCl_2 , CrCl_2 or NiCl_2 .

A considerable degree of stereospecificity is observed in the reaction. The formation of α -methylstilbenes made this observation possible. The methyl NMR bands of these compounds are well separated from those of the other reaction products, and therefore crude hexane extracts of the reaction mixture could be directly measured.

Figure 1 represents NMR band intensity measurements (per proton) of the

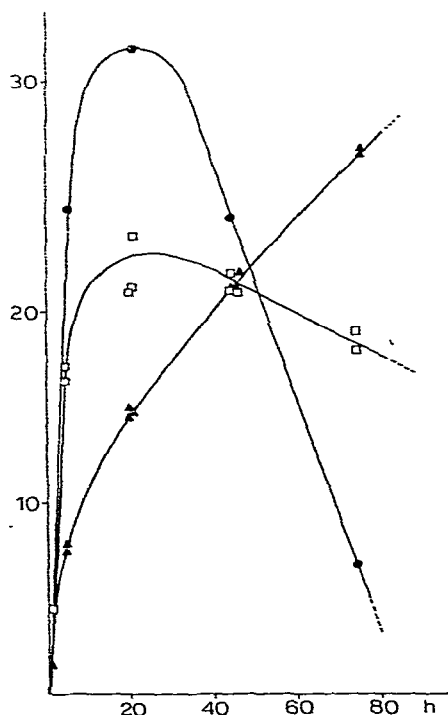


Fig. 1. Reaction profile at $18 \pm 2^\circ$. $\square$ *cis*- α -Methylstilbene, $\blacktriangle$ *trans*- α -methylstilbene, $\bullet$ α -benzylstyrene. The abscissa represents the area integration scale for the NMR peaks at 7.82, 7.78 and 6.2 τ respectively. The count is corrected per hydrogen, *p,p'*-bitolyl was used as an internal standard.

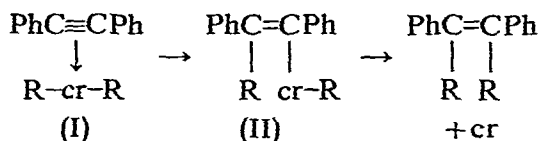
methyl hydrogen of *cis*- and *trans*- α -methylstilbene, and the benzylic protons of α -benzylstyrene, at different reaction times. Evidently, α -methylstilbene is formed initially as the *cis* isomer and consequently isomerizes to the *trans* form. Thus transfer of methyl groups and hydrogen to the alkynes involves a sterically controlled step. Similarly, the preferred formation of *cis*-stilbene was observed by VPC analysis but the complexity of the product mixture hindered satisfactory quantitative measurements. Processes of *cis* to *trans* isomerization under transition metal catalysis have been observed before⁶.

The curve for α -benzylstyrene shows a sharp maximum with relatively rapid increase and decrease in concentration. It could be an intermediate in the *cis*, *trans* isomerization of methylstilbene as has been actually demonstrated for the isomerization in very basic solutions⁷. However, it could also be the precursor of the methylstilbenes and condensation products like tetraphenylbenzene², or polymers. The present results do not admit a simple interpretation.

Transfer of both hydrogen atoms or methyl groups can be explained by the so-called insertion mechanism* assuming the presence of σ -bonded methylchromium and hydridochromium species I (Scheme A) and would involve the formation of transient σ -bonded intermediates (II).

* For a general review see ref. 8.

Scheme A

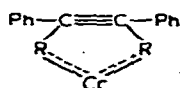


(cr = Chromium and part of its valencies; R = CH₃-, H, CH₂=)

A complex having a structure very similar to II, has recently been isolated as an intermediate in the *cis*-hydrogenation of diphenylacetylene by hydrido-iridium complexes⁹. *cis*-Stilbene was obtained from this intermediate by hydrolysis. Since in our case, formation of products is obviously completed before hydrolysis is effected (Fig. 1) our case is probably different, regarding the last step.

The possibility that the products would form from II, by an intermolecular pathway, i.e. reaction of II with other complex molecules, is expected to lead to the formation of *trans* isomers¹⁰ which is in contrast to our results.

A concerted reaction pathway III, of the type suggested for hydrogenation with RhCl[P(Ph)₃]₂H₂¹¹ is more likely. *cis*-Addition, in such case, is expected and involves the least sterically hindered conformations during the process.



(III)

The formation of benzylstyrene, if it were directly formed, could involve a similar transition state preceded or accompanied by tautomerization of the methylic hydrogen onto the metal atoms, thus forming transient hydrido-chromium derivatives. Carbon to metal tautomerization processes¹², and some evidence for the existence of unstable organochromhydride intermediates¹³ have been described.

Hence in III, R may be CH₃, H, or CH₂: σ -bonded methyl derivatives of transition metals, and the corresponding hydrides are thought to behave similarly¹⁴ on several occasions. The present chromium derivative could not be isolated. It is therefore noteworthy that phenylchromium derivatives, which are isolable, reacted with several alkenes and alkynes, whereby phenyl groups and hydrogen were transferred and addition products formed¹⁵. In one case at least *cis*-addition has been observed.

EXPERIMENTAL

Materials

Tetrahydrofuran (U.C.B. solvent for analysis) refluxed over sodium was distilled and kept over LiAlH₄ and freshly distilled before use. Diphenylacetylene was obtained from Fluka A.G. and used as such*. Chromium trichloride was a sublimed product of Riedel-DeHaen, Hannover, and was used in the form of the tris(tetrahydrofuranate) complex¹⁶. The materials were kept under a nitrogen atmosphere. All apparatus were dried at 120° and cooled under dry nitrogen.

* Tests for impurities in diphenylacetylene were carried out using FID gas chromatography. Impurities of *trans*- and *cis*-stilbene made up several ppm.

The concentrations of solution of the Grignard reagent, CH_3MgX , were checked by both acid base titration and volumetrically.

Instruments

A Varian HA-60-IL NMR spectrometer was used. Vapor phase chromatography was carried out on a 5750 F&M instrument equipped with TC and FID detectors. Mass spectra were carried out on a CEC 21-104 and CEC 21-110B spectrometer.

Reaction of diphenylacetylene and the methylchromium systems

Methylmagnesium chloride in THF* solution (31.5 moles) was added to 10.5 mmoles of finely powdered $\text{CrCl}_3 \cdot 3\text{THF}$ and kept at -70° under a stream of dry nitrogen. A brown slurry formed immediately. Addition of THF facilitated stirring.

The mixture was then allowed to warm to -35° at which temperature 0.56 grams (3.15 mmoles) of diphenylacetylene in 100 ml THF were added over a period of 2.5 h. The slurry was left under nitrogen at room temperature for 40–70 h. When warming up to room temperature, gas evolution was observed. Hydrolysis was carried out with a dilute acid and the products extracted with ether or benzene. Some undissolved hexaphenylbenzene could be collected at this stage. The yellow oils obtained from the ether extract were separated by chromatography. When larger proportions of diphenylacetylene were used, the excess was recovered unchanged.

Similar experiments have been repeated with equivalent quantities of anhydrous CrCl_2 , NiCl_2 and CoCl_2 . Formation of stilbene and methylated products were observed in all these cases.

Attempted reactions with other reagents

10 ml of methylmagnesium chloride ($14 \cdot 10^{-3}$ moles) in THF solution were mixed at room temperature with 2.5 grams of diphenylacetylene ($14 \cdot 10^{-3}$ moles). After 72 h under nitrogen atmosphere, at room temperature, the mixture was hydrolyzed with dilute acid and extracted with ether. VPC and NMR analyses showed the presence of diphenylacetylene only.

A similar test with the proper amount of methyllithium in ether showed no evidence of reaction. Trilithium hexamethylchromium dioxanate complex was prepared⁵ and about 300 mg allowed to react with 100 mg of diphenylacetylene at room temperature. The results were likewise negative. However, some reaction was observed, since after addition of the alkyne, the original bright red color changed within 2 h into dark violet. That color persisted for 48 h and then vanished upon hydrolysis.

Isolation of products

Separation of addition products from the condensation products was carried out by chromatography with n-hexane on silica or alumina columns. The addition products were eluted first, and were separated further by chromatography on activated alumina-preconditioned at 120° , with n-hexane. The eluants were examined by VPC analysis; and final separations, if necessary, were carried out by the latter system.

* Ether or benzene were also satisfactory.

Isothermal analysis at 150° with 10% UC-W-98 silicon columns resolved the mixture in the order: dibenzyl + *cis*-stilbene; *cis*-methylstilbene; α -benzylstyrene; diphenylacetylene; *trans*-stilbene + *trans*-methylstilbene. A different pattern of separation could be obtained with an 6% XF-1500 cyanosilicon column.

Thin layer chromatography was carried out on Kieselgel G (Merck) layers with light petroleum or n-hexane as developer. Iodine, sulphuric acid and UV illumination were used for detection.

Yields were determined from the NMR spectra or by VPC, depending on individual cases.

*Preparation of trans- α -methylstilbene*¹⁷

CH_3MgBr was added to an equivalent amount of desoxybenzoin in THF, and the solution hydrolyzed after 1 h. The products were extracted with hexane and chromatographed on alumina. Desoxybenzoin and some methylstilbene were eluted with hexane, after which an oil—mostly 1,2-diphenylpropanol-2—was eluted with benzene. The neat oil was dehydrated with KHSO_4 , (freshly dehydrated), washed with water and extracted with CCl_4 . Evaporation leaves the crystalline product, which is recrystallized from ethanol. M.p. 81°, NMR data for $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$: 7.78 (doublet) (methyl protons), 3.25 (unresolved quartet) (vinyl protons), 2.75 τ (multiplet); 3:1:10.

MASS SPECTRA

<i>m/e</i>	% base peak	assignment
195	100	$\text{C}_{15}\text{H}_{14}=\text{M}$
179	76	$[\text{M}-\text{CH}_3]^+$
115	32.7	$[\text{M}-\text{PhH}_2]^+$
103	15.3	$[\text{M}-\text{PhCH}_2]^+$
91	14.8	
78	14.8	
52	9.8	

cis- α -Methyl stilbene

The *trans* isomer was irradiated under nitrogen¹⁸ for 8 h in hexane solution. A "Hanau" high pressure mercury c vapor lamp was used, with a quartz filter. The resulting *cis* and *trans* mixture was separated and collected by VPC on a 1/4" 5' 10% SE 30 column at 180° or 10% UC-95 column at 150°. The *cis* isomer (yield 50%) consisted of low melting white crystals. NMR data: 7.82 (doublet), 3.61 (multiplet), 3.1 and 2.88 τ (multiplets); 3:1:10. The mass spectrum is the same as that of the *trans* isomer.

9-Methylphenanthrene

This compound was obtained by repeating the preceding procedure under a stream of air¹⁸ and separated by VPC as above.

1,2-Diphenylpropane

400 mg (2.2 mmoles) of *trans- α -methylstilbene* was added in a hexane solution to a hexane-alcohol slurry of Raney nickel (Fluka) in a hydrogen atmosphere. Hydro-

gen up-take was fast, and after 1 h the solution was filtered and evaporated five times from CCl_4 . No starting material was left, and a single product was obtained (VPC). NMR data: 2.98 (multiplet), 7.25 (multiplet), 8.84 τ (doublet); 10:3:3.

α -Benzylstyrene

Triphenylphosphonium methylene was prepared by the reaction of equivalent amounts of butyllithium and methyl triphenylphosphonium bromide¹⁹ in ether. An ethereal solution of desoxybenzoin was then added in equivalent amounts. A white solid precipitated immediately. After one hour reflux, the solution was filtered and evaporated. The yellow oil was chromatographed on alumina to yield a colorless liquid. NMR data for $\text{C}_6\text{H}_5\text{CH}_2\text{C}(=\text{CH}_2)\text{C}_6\text{H}_5$: 2.8 (aryl protons), 4.63, 5.1 (vinylic protons) (complex patterns), 6.27 (benzylic protons) (broad singlet); 10:1:1:2. Patterns were easily resolved by double irradiations.

MASS SPECTRA

<i>m/e</i>	% base peak	assignment
194	64.5	$\text{C}_{15}\text{H}_{14}=\text{M}$
179	36.3	$[\text{M}-\text{CH}_3]^+$
116	66.4	$[\text{M}-\text{PhH}]^+$
103	100	$[\text{M}-\text{PhCH}_2]^+$
91	42.5	
77	70.8	
51	54.0	

Unlike α -methylstilbene, the cleavage between the α and α' carbons is much enhanced in this case (*m/e* 103), which is not surprising. Other trivial differences as compared to methylstilbenes are also noted, like large intensities of the tropylium and benzenonium ions.

Reaction profile (Fig. 1)

A run was carried out as specified above except for using a large excess (30 mmoles) of diphenylacetylene. The excess was recovered unchanged. The reaction was kept at 18° for 140 h. Equal samples were taken out after 2, 24, 48, 72 and 138 h of reaction, hydrolyzed and extracted with hexane, and evaporated. Generally hexane extraction leaves out most of the hexaphenylbenzene and oils. This facilitated subsequent separation and spectral studies. CCl_4 solutions of those samples were tested by VPC and NMR to obtain product ratios and relative yields. *p,p'*-Bitolyl was used as an internal standard.

ACKNOWLEDGEMENT

We thank Mr. W. HESS for technical assistance. We are also indebted to Dr. C. J. TIMMONS, Nottingham, for a sample of α -methylstilbene, and to Dr. M. HESSE, Zürich, for the mass spectra.

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