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CYCLIZATION OF DIPHENYLACETYLENE ON METHYLCHROMIUM σ-COMPLEXES

III*. HYDROGEN TRANSFER REACTIONS**

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SUMMARY

The reaction of diphenylacetylene with methylchromium systems yields *cis*- and *trans*-stilbene, *cis*- and *trans*-α-methylstilbene, α-benzylstyrene and bibenzyl as well as cyclic and linear condensation products. Studies with a specifically deuterated methylchromium system and diphenylacetylene and also experiments with deuterium oxide have established that the methyl group is the chief source of hydrogen in the formation of these products. Secondary hydrogen sources are also indicated. Transient carbene–chromium complexes are probable intermediates.

INTRODUCTION

Catalyzed hydrogen transfer reactions have been extensively studied in recent years[1,2] in which rearrangements of σ-bonded organometallic compounds to hydrido–metal derivatives are observed. These are rationalized in terms of tautomerization of hydrogen between the carbon atom of the organic substituent and the metal center. Examples are the well-known reaction of ethylene with platinum hydrides in which a reversible addition–elimination has been demonstrated[3], the oxidation of alcohols by iridium complexes[4], tautomerization in phosphine and arsine complexes[5,6] and also reactions of alkylchromium derivatives[7]. Alkylation of olefins with mercury compounds and transition metal catalysts were also shown to involve hydrogen shifts[8].

Among the several types of reactions in this category there are processes which involve "α-interaction"[9]. This is related to the reactivity of C–H bonds at the carbon directly attached to the metal in σ-alkylmetallic compounds. The reaction of diphenylacetylene with σ-methylchromium complexes[10,11] affords a unique opportunity to investigate hydrogen transfer processes of the "α-interaction" type and the role of the transition metal catalyst. The origin of the hydrogen and the products to which it has been transferred can be traced by deuterium labelling. Although the reaction system is complicated, several unambiguous conclusions can be drawn from this study.

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* For Part II see ref. 11.

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RESULTS

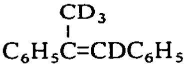
The reaction of the (trideuteromethyl)chromium system was carried out in the usual manner[10,11]. The monomeric products were collected by VPC and analyzed by mass spectrometry. The results are summarized in Table 1. It is evident that the methyl group is the major source of hydrogen (deuterium) in the products. Hydrogen atoms originally in this group are relocated at the vinylic and aliphatic positions of the addition products, providing a clear example of "α-interaction".

TABLE 1

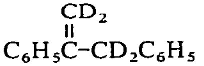
REACTIONS OF $C_6H_5C{\equiv}CC_6H_5$ WITH [$CD_3MgI+CrCl_3 \cdot 3THF$]; DISTRIBUTION OF DEUTERATED SPECIES (%) corrected for natural relative abundances.

Product	D_0	D_1	D_2	D_3	D_4	D_5	D_6
cis-Stilbene	35.19	21.90	41.97	0.94			
trans-Stilbene	18.71	19.58	57.67	2.76	1.28		
cis-α-Methylstilbene	12.86	21.68	8.34	11.58	44.42	1.12	
trans-α-Methylstilbene	6.87	9.63	7.41	21.68	52.01	2.40	
α-Benzylstyrene	26.17	37.25	14.63	13.57	9.87	0.37	0.14

$C_6H_5CD{=}CDC_6H_5$



$C_6H_5\overset{\overset{CD_3}{|}}{C}{=}CDC_6H_5$



$C_6H_5\overset{\overset{CD_2}{\|}}{C}{-}CD_2C_6H_5$

However, isotopic dilution was more extensive than anticipated. The appearance of hydrogen as well as deuterium atoms at vinylic positions in the stilbenes and methylstilbenes clearly requires a secondary source of hydrogen. Extensive dilution observed in benzylstyrene points up the lability of its methylenic hydrogen, verified by hydrogen–deuterium exchange when chromatographed on a VPC column pretreated with D_2O. From the fact that little or no more highly deuterated species (D_3 and D_4 for the stilbenes, D_5 and D_6 for the methylstilbenes and benzylstyrene) were found, it is concluded that the aliphatic and vinylic carbon atoms only are involved in the hydrogen–deuterium exchanges. The absence of aromatic hydrogen–deuterium exchange is substantiated by comparison of the NMR spectrum of *cis*-stilbene collected from a labelled run and the spectrum of an unlabelled sample (see *Experimental*). The resonance intensity of the vinylic protons indicated 60–65% deuteration at the vinylic positions; and this is in agreement with the results from mass spectrometry (53%).

It is noted that *trans*-stilbene and *trans*-α-methylstilbene are richer in deuterium than the corresponding *cis*-isomers. This would appear to be due to progressive hydrogen–deuterium exchange during isomerization at the expense of the *cis*-isomers or to their formation by independent routes.

Water was also examined as a hydrogen source since the potential alkenes conceivably might remain bonded to chromium at the stage of hydrolysis. To this end a similar run was carried out with non-labelled Grignard reagent and the reaction mixture was treated with D_2O. Since σ-bonded alkylchromium compounds are known to undergo fragmentation, demonstrated by the decrease of deuteroalkane obtained by D_2O decomposition of alkylchromium preparations of increasing age[7], the methylchromium system was treated with D_2O after 2, 6, 22 and 56 hours of reaction. Analytical spectra, IR and NMR, failed to detect clearly the presence of deuterium in *cis*-stilbene and *cis*-α-methylstilbene. Mass spectrographic analysis indicated only 8–10% monodeutero-*cis*-α-methylstilbene and ca. 2% in *cis*-stilbene and bibenzyl. In all cases the level of deuteration remained unchanged with time. It is concluded that the hydrolysis step is not a significant source of hydrogen.

Another possible source of hydrogen arises from the observation that gaseous hydrogen is evolved during reaction[12]. A run was therefore made in an atmosphere of hydrogen and the system was indeed influenced. The incorporation of hydrogen was shown by increased yields of the hydrogenation products, *cis*-stilbene and bibenzyl.

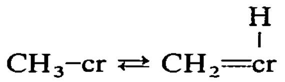
However, additional secondary hydrogen sources are required to account for the extensive isotopic dilution; and, since hydrolysis provides little or no hydrogen for this purpose, the participation of α-hydrogen from *ligand* tetrahydrofuran is conceivably well suited to this purpose. An analogy is found in metal complexes having phosphine ligands[5].

DISCUSSION

Reaction mechanisms for hydrogen transfer in organometallic complexes have been discussed. A relevant example would be the well-known insertion mechanism* pertaining to the reaction of diphenylacetylene with iridium hydrides[14]. Other examples reported involve a hydrogen traverse from a metal-bonded alkyl group to an unsaturated ligand without intermediate contact with the metal center[15–17]. The methylchromium system almost certainly differs from the methylcobalt complex in which methyl radicals were formed[18].

The methylchromium system is believed to give rise to transient metal hydrides in the reaction with diphenylacetylene, and recent work supports this contention. Fragmenting alkylchromium compounds, when treated with deuterium oxide generate hydrogen deuteride in the gaseous products[7]. This result has been observed with methylchromium and (trideuteromethyl)chromium systems[12]. The resemblance in the pattern of transmethylation and hydrogen transfer can be interpreted in terms of similar mechanisms.

It is concluded, therefore, that the transfer of hydrogen (or deuterium) from methyl groups to chromium provides an active hydridochromium intermediate for subsequent hydrogenation reactions with diphenylacetylene. This transfer generates methylene–chromium (carbene–chromium) for synthesis of cyclic condensation products[11].



$$\mathrm{CH_3{-}cr} \rightleftarrows \mathrm{CH_2{=}}\overset{\mathrm{H}}{\overset{|}{\mathrm{cr}}}$$

Carbene–chromium compounds are well established[19] and the occurrence of carbene entities has been recognized in chromium-catalyzed reactions[20]. Consequently a

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* For a general review see ref. 13.

transitory species containing :CH_2 linked to chromium appears rational. Deuterolytic studies of reaction and hydrolysis gases support this view[12].

EXPERIMENTAL

Reaction with deuterated methyl substituents

The reaction of the (trideuteromethyl)chromium system with diphenylacetylene was carried out by the usual procedure[10]. The final reaction mixture was hydrolyzed after 20 h at room temperature, extracted with hexane and the olefins, stilbene, α-methylstilbene and α-benzylstyrene were collected by VPC directly from that extract. By collecting directly from the crude extract, contamination of *cis*-stilbene with bibenzyl could not be avoided, but direct isolation was preferred in order to avoid possible loss of deuterium. $6'\frac{1}{4}''$ columns of 10% UC-W-98 silicon rubber at 150° or 10% SE 30 silicon at 180° were used. A control experiment with CH_3MgI was run for 65 h and the products were collected in the same way. The compounds thus obtained, from both runs, were analyzed by mass spectrometry. The values of mass distribution in the labelled substances, corrected for natural abundance, are presented in Table 1.

Analysis of deuterated stilbene by NMR

The NMR spectra of *cis*-stilbene from the labelled run and from the control run were compared. The last one contained 8% of bibenzyl according to the methylene band at δ 2.87. The aromatic resonance bands of the two compounds are overlapping and the proper correction for bibenzyl present, is necessary. The spectrum of the labelled sample had a ratio of 14.2 to 1 of the aromatic band (δ 7.64) to the vinylic band (δ 6.52). There was only a trace of absorption at δ 2.87. However, allowance was made for a maximum of 8% bibenzyl (which might be deuterated at the aliphatic positions). Taking this into account, the extent of deuteration at the α-positions of stilbene is estimated to be ~62%.

TABLE 2

NMR SPECTRA OF *cis*-STILBENE

δ (ppm)	Integration values		Assignment
	Deuterated	Control	
7.64	142	65	Vinylic H
6.52	10	12	Aromatic H
2.87[a]	—	2	

[a] Traces of bibenzyl.

TABLE 3

MASS SPECTRA

Corrected for natural abundance.

Assignment	m/e	%
$C_{15}H_{14}$	194	89.0
$C_{15}H_{13}D$	195	10.1
$C_{15}H_{12}D_2$	196	0.9
		100.0

Deuterium exchange on the VPC column

The column was flushed four times with 250 μl D_2O and 50 μl of α-benzylstyrene injected once and collected. Operation conditions were as cited above.

Reaction with D_2O

From the reaction mixture, pairs of samples were taken out at predetermined times, one was treated with water, the other with deuterium oxide. The products were isolated and collected according to the procedures described above. Infrared and NMR spectra failed to detect the presence of deuterium in *cis*-stilbene and *cis*-α-methylstilbene. The mass spectrometric analysis indicated only 8–10% of monodeuteromethylstilbene and a few percent of deuterostilbene. The level of deuteration did not change whether 2, 6, 22 or 56 h were allowed for reaction.

Reactions under an atmosphere of hydrogen

The procedures were the same as above except for a different atmosphere. The gas was oxygen-free and dry. The hexane extracts were evaporated and the residue dissolved and evaporated several times from CCl_4. NMR spectra of those crude CCl_4 solutions, were used for the estimation of yields. In a representative run, the yield of bibenzyl after an 18 h reaction under hydrogen was eight times higher than the yield from an 48 h reaction under nitrogen. In the same run the yield of *cis*-stilbene was increased by 50% under a hydrogen atmosphere.

Materials and instrumentation

CD_3I (99%) and D_2O (99.7%) were purchased from Ciba AG, Basel. A Varian A60 spectrometer and a Perkin–Elmer 21 IR spectrometer were used. Mass spectra were obtained with a CED 21-104 instrument. Spectra were taken in CCl_4 solutions. For VPC, a F&M model equipped with flame and TC detectors was used.

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