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CYCLIZATION OF DIPHENYLACETYLENE ON METHYLCHROMIUM σ-COMPLEXES
IV. GASEOUS PRODUCTS

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SUMMARY

CD_3MgI and $CrCl_3(THF)_3$ react at −70° to give a reagent which on warming to 20° fragments giving mainly CD_3H, together with 14% CD_2H_2. Hydrolysis of the resulting mixture produces CD_3H and some HD. These observations are considered in relation to the interaction of the methyl–chromium reagent with diphenylacetylene.

INTRODUCTION

The reaction of a methylchromium reagent (prepared from methylmagnesium chloride and chromium trichloride tris(tetrahydrofuranate) with diphenylacetylene[1−3] gives, among many other products, stilbenes and methylstilbenes. It was suggested that these were formed from chromium-bound methyl groups, the former via a chromium–hydride intermediate, since it was shown[3] that little or no hydrogen is incorporated during hydrolysis. Furthermore, it was found that when the methylchromium reagent was formed from CD_3MgI, the stilbenes and methylstilbenes contained a high proportion of deuterium. The actual amount of deuterium incorporated was, however, less than expected if transfer of a methyl group and a hydrogen originating from such a group were the only processes occurring. Hydrogen exchange with the solvent was suggested as the cause of the discrepancy.

The observation that during the reaction gas is evolved as the mixture is warmed to room temperature suggests that the reagent slowly disintegrates (it is unstable at room temperature) and that a study of this gas might throw more light on the reactions occurring. Accordingly, both the non-condensable (−196°) gas resulting from the disintegration of the methyl-d_3 chromium reagent in the presence of diphenylacetylene in diethyl ether/tetrahydrofuran and that from hydrolysis of the final reaction mixture were collected and analyzed by mass spectrometry.

RESULTS AND DISCUSSION

The results are presented in Table 1.

The CD H in the reaction gas must arise by rupture of the Cr–C bond and

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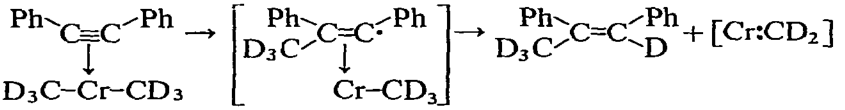
TABLE 1

COMPOSITION OF GASES

Compund	Reaction gas (%)	Hydrolysis gas (%)
CD_4	0.18	3.78
CD_3H	81.25	83.48
CD_2H_2	14.00	1.23
CH_4		4.11
DH	0.34	7.41
H_2	4.23	[a]

[a] The hydrolysis gas contained 52.97% hydrogen. Since hydrogen is known[4] to be formed by the action of water on reduced chromium species, this cannot be taken to indicate a large concentration of Cr–H bonds in the mixture, and the figures have been corrected to zero % hydrogen. Both sets of figures have been corrected for traces of air.

subsequent attack on the solvent. This rupture may be occasioned by the displacement of stabilizing THF ligands by PhC≡CPh[5]. If the CD_3 species liberated (or partially liberated) by disintegration of the Cr–C bond attacks the diphenylacetylene, then the pathway to methylstilbenes is opened, as represented schematically in eqn. (1):



(1)

where Cr represents the chromium and remaining chromium-bound ligands.

The high concentration of CD_3H in the hydrolysis gas implies that little isotope exchange can occur in the methyl group bound to chromium. On the other hand the high proportion of CD_2H_2 in the reaction gas argues that removal of deuterium from CD_3 is important, and that some of this deuterium becomes bound to the chromium is indicated by the high proportion of HD found in the hydrolysis gas.

$$[D_3C\text{–}Cr] \rightarrow [D\text{–}Cr{:}CD_2] \qquad (2)$$

Stable chromium–carbene complexes are well known* and a transitory species containing $:CD_2$ linked to chromium does not seem improbable. That it is highly reactive is shown by the small amount of CD_2H_2 formed on hydrolysis. Reaction with the solvent must produce CD_2H_2 during the reaction. Reaction with PhC≡CPh and subsequent attack on the solvent by the reactive species so-formed would give isotope-diluted products. Formation of HD on hydrolysis indicates that the Cr–D bond is less reactive than $[Cr{:}CD_2]$ and an appreciable amount survives until the moment of hydrolysis. The small quantity of HD in the reaction gases shows that Cr–D bonds are not susceptible to attack by the solvent to any great extent.

EXPERIMENTAL (with Mr. W. Hess)

$CrCl_3(THF)_3$ (862 mg) was weighed into a flask, and PhC≡CPh (178 mg), CD_3MgI (8.3 ml of 9.2 mmolar solution in Et_2O) and THF (15 ml) were sealed in a

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* See for example ref. 6.

bulb attached by a rotatable joint to this flask. The two vessels were degassed three times under high vacuum, and the reagents mixed. The gas evolved was pumped through a −196° trap and the non-condensed material sealed in an ampoule and analyzed by mass spectrometry (CEC 21-104).

In one case using 9.2 mmole of CD_3MgI, approximately 4 mmole of gas was obtained during the reaction, but amounts varied somewhat. When no more gas was evolved, the reaction mixture was hydrolyzed with degassed H_2O and the gas evolved treated as before. The liquid phase was extracted with Et_2O and analyzed by GLC (see reference 2 for details), which showed that the reaction had proceeded in the usual way.

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