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Preliminary communication

EVIDENCE FOR REVERSIBLE ATTACK OF A CARBANION ON AN η^6-ARENETRICARBONYLCHROMIUM(0) COMPLEX

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Summary

The regioselectivity of the reaction between 2-lithio-2-methylpropionitrile and η^6-1-methyl-1,2,3,4-tetrahydroquinolinetricarbonylchromium(0) was found to be time- and temperature-dependent. Reaction at −70°C yielded initially three regioisomers in the ratio 35/64/1. On prolonged reaction time or warming, equilibration gave the same three isomers but in the ratio 2/96/1.

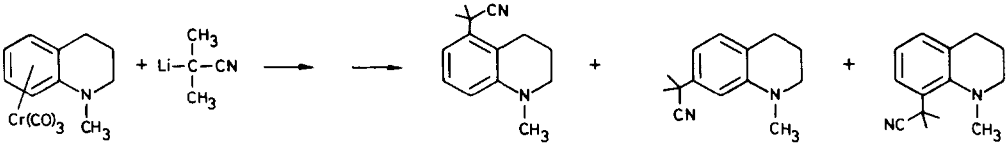
The question of kinetic vs. thermodynamic control in the distribution of regioisomeric products arising from substitution of arenetricarbonylchromium complexes by carbanions has not generally been considered. Kinetic control is generally assumed to predominate [1].

We have prepared η^6-1-methyl-1,2,3,4-tetrahydroquinolinetricarbonylchromium(0) (1) and studied its reaction with 2-lithio-2-methylpropionitrile (2). We find that the product isomer distribution depends on the reaction time and temperature in a way consistent with equilibration of the initially formed products, leading to essentially quantitative formation of one regioisomer at thermodynamic control.

In a typical reaction a solution of complex 1 (1.17 mmol) (prepared according to standard procedures [2]) in cold THF (10 ml, −70°C) was added to a solution of 2 (1.43 mmol) in THF (10 ml, −70°C). The mixture was stirred for the time specified in Table 1. A precooled solution of iodine (7 mmol) in THF (10 ml, −70°C) was then added, the mixture was allowed to warm to 20°C during 1 h, and the organic products were isolated by conventional extraction procedures. The crude product mixtures were analysed by GC/MS.

The total yield of isomers 3, 4 and 5 was found to be high (>95% according to GC). The yield of regioisomer 5 was always low, but reproducible. However, the relative ratio of 3 and 4 was found to vary from 35/65 (−70°C/1 min) to

2/97 (—70°C/8.6 h). Carefully controlled experiments were undertaken to study the time/temperature dependence of the reaction. Representative results are summarized in Table 1.



1 2 3 4 5

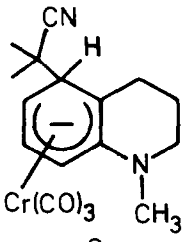
TABLE 1

REGIOISOMERIC PRODUCTS 3, 4, AND 5 WERE OBTAINED FROM SEQUENTIAL TREATMENT OF η^6-1-METHYL-1,2,3,4-TETRAHYDROQUINOLINETRICARBONYLCHROMIUM(0) IN THF AT —70°C WITH 2-LITHIO-2-METHYLPROPIONITRILE FOLLOWED BY IODINE. THE RELATIVE YIELDS WERE BASED ON GC/MS ANALYSES

Reaction time	Relative yields of regioisomers		
	3	4	5
1 min	35	64	1
2 min	33	66	1
6 min	27	73	0
8.6 h	2	97	1
2 min [a]	44	55	1
15 min [a]	44	54	2
22 h [a]	44	54	2

[a] In the presence of 4 eq. of HMPA.

Nucleophilic attack on 1 by stabilized carbanions is predicted to occur at positions 5 and 7 by analogy with results obtained for other nitrogen and oxygen substituted η^6-arene-Cr(CO)$_3$ complexes for which the *meta*-directing effect of donor substituents has been amply demonstrated [3]. The ratios of regioisomeric products obtained after oxidative work up are generally considered to be kinetically controlled [4]. Inspection of Table 1 shows that the unpredicted isomer 5 is formed in a low but constant yield. Isomers 3 and 4 are the major components after short reaction times, as predicted. Their ratio during the first few minutes is assumed to reflect rather closely the kinetic control of the nucleophilic attack on 1. However, the change in relative ratio of 3 and 4 with time indicates the onset of thermodynamic control the more crowded intermediate anion 6 being converted into the more favoured 7.



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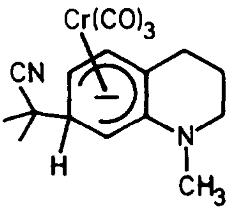

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After prolonged reaction times an equilibrium is reached, the 7-substituted regioisomer 4 being then strongly favoured (Table 1).

There is some precedent for the equilibration of cyclohexadienyl-$Cr(CO)_3$ anion intermediates. For example in nucleophilic attack on η^6-chlorobenzene-$Cr(CO)_3$ the product distribution depends on reaction time [3b,5].

The equilibration of intermdiates 6 and 7 can be thought of as an intramolecular process, i.e. a 1,5-sigmatropic shift of the 2-[2-methylpropionitrile] group.

$$6 \rightleftharpoons 7 \tag{1}$$

Alternatively, the nucleophilic attack on 1 could be reversible, leading to equilibration of 6 and 7 via the starting materials.

$$6 \rightleftharpoons 1 + 2 \rightleftharpoons 7 \tag{2}$$

In order to differentiate between the two mechanisms the reaction was carried out in the presence of HMPA, which is expected to coordinate strongly to the lithium cation (cf. Table 1). For the intramolecular rearrangement process (eq. 1) coordination of the counterion is not expected to influence the equilibration of 6 and 7. However, if the nucleophilic attack is reversible (eq. 2) some effect could be expected. As seen from Table 1 addition of four equivalents of HMPA leads to a constant mixture of regioisomers 3 (44%) and 4 (54%). The relative yields of 3 and 4 obtained in the presence of HMPA can probably be assumed to reflect true kinetic control of the nucleophilic addition and the attack would thus be irreversible in this medium. This is consistent with the formation of a higher-energy "naked" isobutyronitrile anion on solvation of lithium by HMPA.

Thus, in conclusion, we have observed an unusual case of a reversible nucleophilic addition to an arene-$Cr(CO)_3$ complex. Further work to investigate the generality of our observation of thermodynamic control is in progress.

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