Novel Reaction of Trialkylalkynylborates with Cationic Metal Complexes

By ANDREW PELTER* and KEN J. GOULD

(*Department of Chemistry, University College of Swansea, Singleton Park, Swansea* SA2 8PP)

and LEON A. P. KANE-MAGUIRE

(*Department of Chemistry, University College of Cardiff, Cathays Park, Cardiff*)

Summary Attack by trialkylalkynylborate salts upon cationic metal complexes proceeds in a stereo- and regiospecific manner to yield novel complexes.

ELECTROPHILIC attack upon trialkylalkynylborates (I) has now been established as an attractive route to highly substituted olefins and ketones.[1] The use of cationic dienyl iron complexes in electrophilic substitution has recently been described[2] and it was thus of interest to examine the interactions of cationic metal complexes with the salts (I). By analogy, it was envisaged that the initial products would be (III), as in the Scheme.

A unique feature would be that the nucleophile would undergo rearrangement during the reaction and the process would be irreversible. By contrast, the products of addition of simple anions to cationic dienyl iron complexes may lose the anions in further reactions.[3]

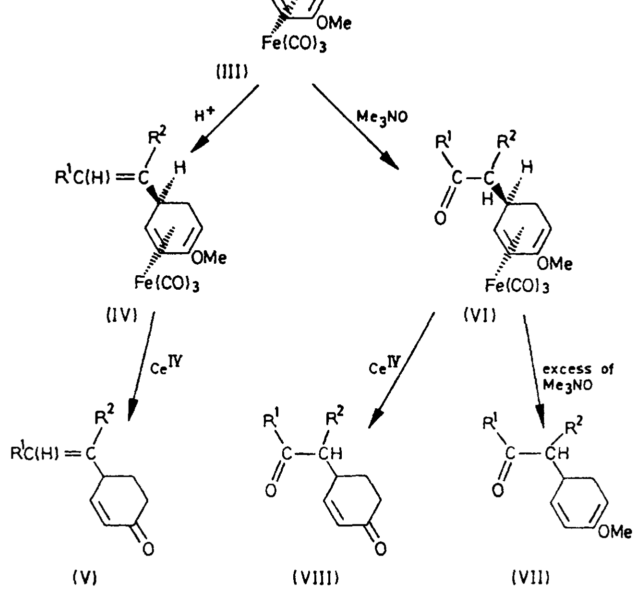
TABLE[a]

Reactions of $[(C_6H_6OMe)Fe(CO)_3]^+BF_4^-$ with $R^1_3\bar{B}CCR^2$

		Hydrolysis products[b]		Oxidation products		
R^1	R^2	(IV)	(V)	(VI)	(VII)	(VIII)
n-Hexyl	Bu^n	77	72	48	46	46
Cyclohexyl	n-Hexyl	79	70			

[a] All yields of pure characterised products. [b] Hydrolysis with isobutyric acid at 25° for 30 min.

In the event, the ready reaction of the tetrafluoroborate (II) with tetrahydrofuran solutions of the borate salts (I) proceeded cleanly according to the Scheme. Hydrolysis of the intermediates (III) with isobutyric acid gave good yields



of the olefinic complexes (IV) (Table) from which the cyclohexenone derivatives (V) were isolated after oxidation with Ce^{IV}.

Oxidation of (III) with anhydrous trimethylamine oxide (4 mol. equiv.)[4] gave the ketonic complexes (VI) from which the diketones (VIII) were produced on oxidation with Ce^{IV}. When the intermediates (III) were oxidised by a large excess of trimethylamine oxide[5] the boron and iron were both removed and the enol ethers (VII) were isolated. When the complexes (III) contain sec-alkyl groups they are resistant to attack by trimethylamine oxide.

It was established by ^1H n.m.r. spectroscopy that attack was both stereo- and regio-specific, the sole products being the *exo*-5-substituted cyclohexadiene derivatives (III). The alkyl migration was not stereospecific as (*Z*)- and (*E*)-olefins (IV) were obtained in the ratio 65:35.

It remains to improve the oxidative removal of the boron atom from the complexes (III). So far the use of MnO_2, Collins reagent,[6] Ce^{IV}, and hydrogen peroxide have proved unsatisfactory and further oxidative processes are being investigated.

These are the first examples of attack by borate salts upon a cationic metal complex. Preliminary investigations using tricarbonyl(cyclohexadienyl)iron tetrafluoroborate, tricarbonyl(tropylium)chromium tetrafluoroborate, and cyclopentadienyl(benzene)iron hexafluorophosphate indicate that a wide variety of cationic complexes undergo attack. Hence the examples reported represent the first of a new class of reaction.

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