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Preliminary communication

REARRANGEMENTS OF ORGANOMETALLIC COMPOUNDS

XI*. DUALITY OF MECHANISM FOR 1,2-ARYL MIGRATIONS IN THE OXIDATION OF TETRAARYLBORATE SALTS

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Summary

Individual oxidative couplings of potassium phenyl(tri-*m*-tolyl)borate and potassium phenyl(tri-*p*-tolyl)borate with transition metal ions, organic oxidants and halogen sources revealed a duality of mechanism, namely electron-transfer and electrophilic pathways. Not only the ratios of the respective bitolyls and methylbiphenyls obtained, but also the behavior of potassium bis(*o,o'*-biphenylene)-borate, showed that bridging of the migrating group is important for iodine oxidations, but not for Ce^{IV} oxidations.

The oxidation of tetraorganoborate salts, either by ceric ion or molecular halogen, constitutes a method of growing significance for forming carbon—carbon bonds. Treatment of lithium trialkyl(alkynyl)borates with iodine has been offered as an excellent route to disubstituted acetylenes [2]. Likewise, both the ceric ion [3] and molecular halogen [4] oxidations of tetraarylborates (I—III) lead to high yields of biaryls. Careful mechanistic studies have demonstrated that both ceric ion and electrochemical oxidations proceed by electron-transfer [5] and that biaryl formation ensues within the borate ion [6]. No evidence is available on the course of halogen oxidations [4, 7].

$$\underset{\text{(I)}}{B(C_6H_5)_4^-} + [O] \xrightarrow{-2e^-} \underset{\text{(II)}}{C_6H_5{-}C_6H_5} + \underset{\text{(III)}}{(C_6H_5)_2B^+}$$

We now wish to report a remarkable reversal of preference in biaryl formation shown in the oxidations of potassium phenyl(tri-*m*-tolyl)borate (IV)

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* For previous parts see refs. 1a, 1b.

TABLE 1

OXIDATIVE COUPLINGS OF POTASSIUM PHENYL(TRI-(*m* OR *p*)-TOLYL)BORATES

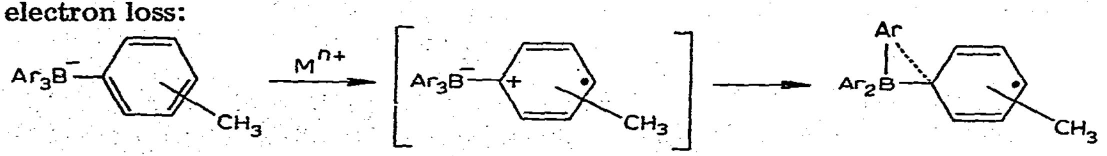
Oxidant[a]	Ratios of ($CH_3C_6H_4—C_6H_4CH_3$) and ($CH_3C_6H_4—C_6H_5$)	
	m-Tolyl isomer (IV)[b]	*p*-Tolyl isomer (V)[b]
I_2	3.4/1.0	1.0/3.3
Br_2	1.8/1.0	1.0/2.4
NBS	1.7/1.0	1.0/2.0
DDQ	1,9/1.0	2.0/1.0
Fe^{3+}	1.4/1.0	2.2/1.0
Ce^{4+}	1.4/1.0	2.5/1.0

[a] The reactions were conducted by dissolving 2.5 mequiv. of oxidant in 25 ml of $CHCl_3$ (I_2, Br_2 and DDQ) or in acetone (Fe^{3+} and $Ce(NH_3)_2{}^{4+}$) or suspending in CCl_4 (NBS); then 1.25 mmol of IV or V (partially soluble) was added. All oxidations were performed at room temperature for 22 h, except with NBS, where heating at reflux was carried out. [b] Satisfactory elemental analyses and NMR spectral proton ratios were obtained for IV, V and VI.

and potassium phenyl(tri-*p*-tolyl)borate (V) that clearly reveals the operation of two different reaction mechanisms. Furthermore, these mechanistic pathways have been shown to have different geometrical constraints by observing whether or not the oxidant can bring about the oxidative coupling of potassium bis(*o,o'*-biphenylene)borate (VI).

The ratios of the respective methylbiphenyl and bitolyl resulting from the oxidation of IV and V, respectively, with transition metal ions (Ce^{4+} and Fe^{3+}), an organic oxidant (DDQ)* and halogen sources (I_2, Br_2 and NBS) were determined by gas chromatography (Table 1). Although the amounts of biaryl formed by halogenative oxidations are quite dependent on the nature of the solvent and the metal gegenion (Li^+, Na^+ or K^+), the ratio is not very sensitive to the extent of reaction. Now, if an electron-transfer process [5, 6] were involved in each oxidation, similar coupling profiles should be displayed for the *para*- and the *meta*-isomers. Instead, with halogen oxidants the *para* salt (V) shows a striking preference to yield *p*-methylbiphenyl. A similar contrast between a known, electron-transfer oxidant, Ce^{4+} and a selective halogenative oxidant, I_2, is their behavior toward the spirobiphenylene borate salt, VI. Ceric ion oxidation and a protodeborative work-up gives a 75% yield of *o,o'*-quaterphenyl; iodine oxidation, on the other hand, gives, in > 90% after the usual protodeborative work-up, a 1/1 mixture of only *o*-iodobiphenyl and biphenyl but no quaterphenyl.

Because of the similarity of the biaryl ratios for the oxidants, Ce^{4+}, Fe^{3+} and DDQ, it is reasonable to conclude that they all operate as electron-transfer agents, as has been well-documented for Ce^{4+} [5, 6]. Preferential formation of the bitolyl from either salt clearly implies that the tolyl group undergoes preferred attack, for a random oxidation would yield a 1/1 biaryl mixture. It is understandable that the tolyl group should be more prone than the phenyl to electron loss:



(VII)

(VIII)

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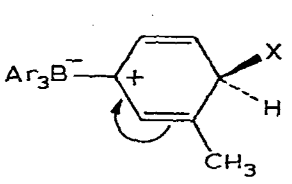
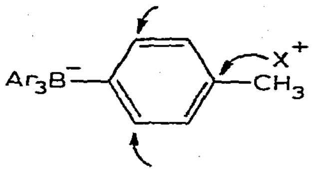
*DDQ = dichlorodicyanoquinone; NBS = *N*-bromosuccinimide.

If aryl migration from boron to carbon [8] (VII → VIII) were completely random, then a maximum of 2/1 in the bitolyl: *p*-methylbiphenyl ratio would be expected. Since the observed ratios (1.4/1.0—2.5/1.0) are within, or only slightly outside of, this maximum, no great migratory preference is revealed in the collapse of VII.

The behavior of the halogenative oxidants, however, cannot be uniformly explained by electron-transfer, but seems to require an electrophilic mechanism. Attack of X^+ on IV generates the electron deficiency α to boron, requisite for migration [8], and at the same time leads to a transition state (IX) stabilized by the methyl group. The biaryl ratio ($>$ 2.0/1.0) shows that iodine not only attacks the *m*-tolyl group selectively, but also that *m*-tolyl subsequently migrates preferentially. With the *para* salt (V), attack by X^+ at the *para* positions of the tolyl groups is seriously hindered, and the alternative attack at the *ortho* positions impeded by, the bulk of the electrophile X. As a consequence, electrophilic attack on the more accessible phenyl group is relatively lower in energy and, accordingly, the formation of *p*-methylbiphenyl is favored.

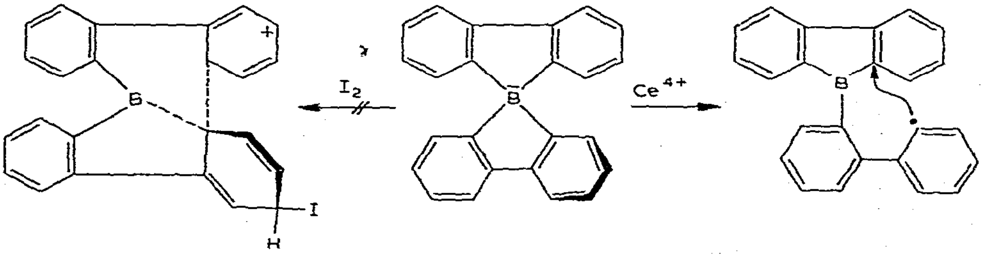


(IX)



(X)

The suggestion of an electrophilic mechanism for iodinative biaryl couplings clarifies the behavior of VI. Since ceric ion oxidation involves electron-transfer with little or no aryl migratory preference, there seems to be no bridging (VIII) in the aryl group migrating from boron to carbon. Hence, radical XI can collapse to yield a quaterphenyl precursor. On the other hand, the attack of I_2 seems to require some bridging of the migrating aryl group (cf. preference of *m*-tolyl migration with IV). But, because of the perpendicular array of the aryl groups in VI, a bridging transition state should be highly strained (VII). Since such bridging would make C—C bond coupling energetically unfavorable, the alternative reaction of simple iododeboration occurs exclusively.



(XII) (VI) (XI)

The interplay of varying electronic and steric factors in these electron-transfer and electrophilic coupling processes should prove to be important in the controlled, selective formation of carbon—carbon bonds.

Acknowledgement

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