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ORGANOELEMENTAL FRAGMENTATIONS

III *. ON THE MECHANISM OF ISOTOPE ENRICHMENT OF THE AROMATIC RING IN ORGANOMETALLIC BENZYL COMPOUNDS WHEN REACTED WITH ACIDS **

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Summary

The β-effect of a metal is mainly exhibited in decomposition of a metal—carbon bond. Nevertheless, there is a well known case in which it was assumed that the metal—carbon bond was retained in the course of electron delocalisation at the adjacent carbocation site. This reaction is isotopically labelled acid cleavage of benzylmercuric chloride, which results in both electrophilic fragmentation (F_E), leading to the 1-methylene-6-deuteriocyclohexadiene-2,4 intermediate, and in hydrogen/deuterium replacement, leading to isotope enrichment of the aromatic ring of the starting species. However, we found that this process is governed by an electrophilic fragmentation, not an electrophilic aromatic substitution, mechanism. The study of deuterio-demetalation of benzylmercuric chloride with deuterium chloride, containing a mercuric chloride additive, has revealed that the demetalation rate and the isotope enrichment rate are markedly dependent on the mercuric chloride concentration in the system. These results, inexplicable in terms of the C—Hg hyperconjugation concept (σ—π conjugation), may suggest that the metal—carbon bond conservation in the process under discussion is only apparent. A new two-step mechanism has been formulated for the reaction under study, based on aromatisational metalation of the *exo*-methylene—cyclohexadiene structures, leading to isotopically labelled benzyl organometallics under the action of metal salts.

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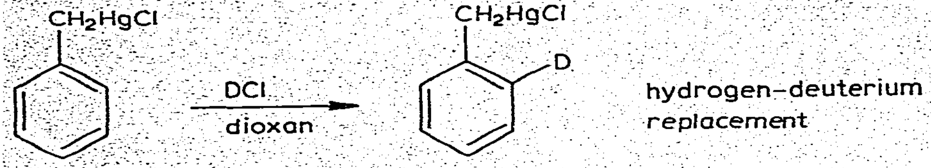
* For parts I and II, see refs. 1 and 2.

** Parts I—III translated by A.V. Grib, NMR Laboratory, Chemistry Department, Moscow University, Moscow B-234, U.S.S.R.

Introduction

Among the numerous reactions of organometallic compounds with electrophiles there is a process, in which the final products suggest that no metal—carbon bond decomposition has occurred. The reaction in question is hydrogen/deuterium replacement in benzyl organometallics, found initially for the reaction of $PhCH_2HgCl$ with DCl [3—10] (eq. 1).

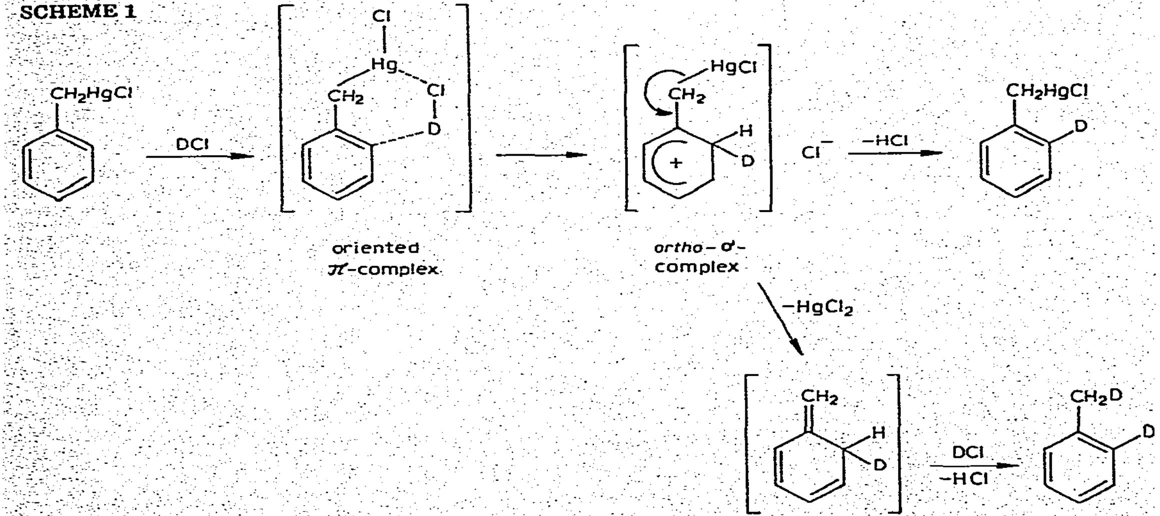


(1)

Similar phenomena were later found for the acid cleavage of benzyl derivatives, $PhCH_2B(OH)_2$, [11]; $(PhCH_2)_2Hg$, [11,12]; σ-$PhCH_2Fe(CO)_2Cp$, [13,14]; σ-$PhCH_2Mo(CO)_3Cp$ and σ-$PhCH_2W(CO)_3Cp$ [15]; of a number of transition and non-transition elements.

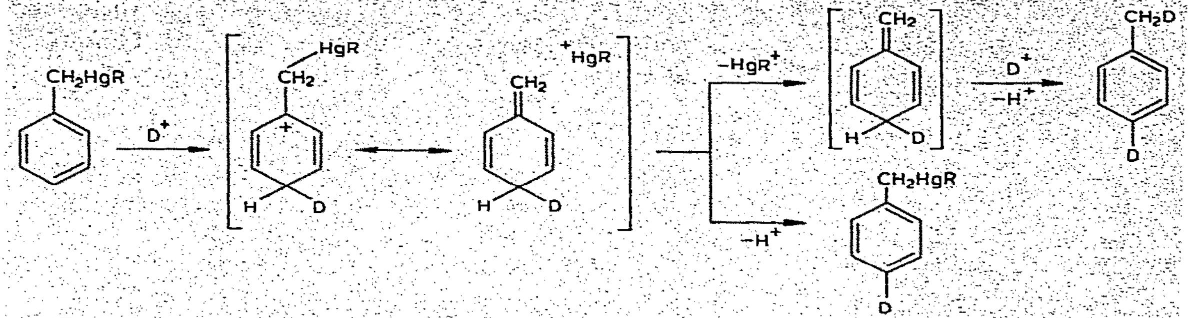
An assumption, made earlier, was that two processes occurring in acid cleavage of $PhCH_2HgCl$ with DCl have a common intermediate. The processes mentioned are demetalation leading to alpha, *o*-dideuteriotoluene and deuteriation of the ring of the starting benzyl compound. As for the intermediate, it is an *ortho*-σ-complex stabilised by σ—π conjugation and capable of decomposing via two competing paths, viz., the loss of metal to form tautomeric toluene and elimination of the proton to result in the isotopically labelled organometallic compound [3—6,9] (Scheme 1).

SCHEME 1



Later, T. Traylor generalised this representation and applied it to hydrogen/deuterium replacement at the *para* position of the benzene ring of $(PhCH_2)_2Hg$ and $PhCH_2B(OH)_2$. He also specified the electron delocalisation nature in σ-complexes of this kind in terms of the hyperconjugation concept [11,12,16] (Scheme 2).

SCHEME 2. "VERTICAL" STABILISATION OF THE CATION CHARGE: σ—π CONJUGATION



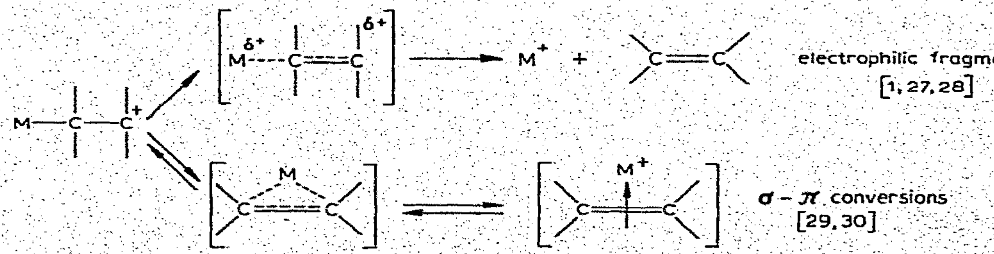
This concept suggests that the ability of benzyl organometallics to enter into hydrogen/deuterium replacement reactions might be due to metal—carbon bond hyperconjugation being much stronger than hyperconjugation of C—H and C—C bonds (cf. [17,18] the Nathan—Baker series).

Today, we may say that the point of view put forward by the writers [3—7, 9] which, as follows from the collation above, does not essentially differ from the concept developed by Professor Traylor [11,12,16], was the only explanation of isotope enrichment of organometallic benzyl compounds in their reactions with acids. The concept, as laid down above, was later supported by other workers [13—15,19,20] and found its place in reviews [21] and monographs [22].

The basic assumption is that the σ-complexes (I) stabilised by σ—π conjugation may exist as kinetically independent species long enough to permit a proton to be eliminated from the position 2 or 4 of the ring, resulting in a hydrogen/deuterium replacement product (eq. 1 in which the M—C bond is not broken) *.

We believe, however, that this assumption does not fit in well with numerous organometallic reactions in which the β-effect of a metal—carbon bond results in just dissociation (β-decomposition [24—26]) of the bond, as far as the simpler three-centre systems of type I are concerned:

SCHEME 3. "NON-VERTICAL" STABILISATION OF β-METALATED CARBOCATIONS



electrophilic fragmentation (F_E) [1,27,28]

σ – π conversions [29,30]

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* Note that some organometallic reactions with electrophiles do involve metal—carbon bond conservation (see, e.g., the monographs [23]). But the C—metal bond does not participate in the transition states of these reactions, so the respective results are quite coherent. In contrast, acid cleavage of benzyl organometallics is brought about by the carbon—metal bond participating in the delocalisation (β-effect). This conclusion is based on the fact that carbon and hydrogen analogues of the benzyl compounds, $PhCH_2$—CH_3 and $PhCH_2$—H, do not exchange their ring hydrogens for deuterium under the same experimental conditions.

Our search for an alternative mechanism stems from just this discrepancy. Indeed, the reactions involving the β-effect of a metal result more often than not in demetalation and olefine formation. Consequently, the metal—carbon hyperconjugation concept may well be done without in these cases (e.g., [20]), since the reactions may be explained as well with any of the traditional "non-vertical" hypotheses (Scheme 3).

The main, if not only, example of a chemical reaction explainable exclusively in terms of carbon—metal hyperconjugation, was isotope enrichment of the ring in benzyl organometallics reacting with acids. If one agrees with this interpretation [3—7,9,11—16,20—22] of the mechanism, this process will be the main chemical proof [*] of the ability of metal—carbon bonds to participate in resonance interactions.

Results and discussion

1. A mechanism of isotope enrichment in the aromatic ring of benzylmercury chloride subject to deuterio-demetalation

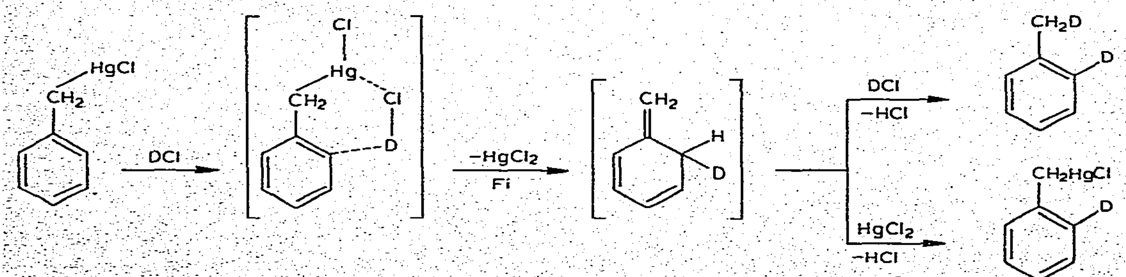
The attempt made in the present paper to find an alternative explanation resolves essentially in answering the question as to how one can specify the metal—carbon bond β-effect in reactions of benzyl organometallics, when compared with simple alkyl models of the type M—C—C$^+$.

It is essential that fragmentation demetalation [1], via the tautomeric arene intermediates, is an accompanying process in all reaction systems where isotope enrichment of the ring is observed in organometallic benzyl compounds. An assumption ia made that the isotope enrichment mechanism is bound just to these intermediates.

Accordingly, there is an essential difference between fragmentations in benzyl organometallics [1,2] and fragmentations in the M—C—C$^+$ systems [24—27]. The former reactions result in tautomeric arenes which are highly reactive in their retro fragmentations, i.e. in electrophilic addition-eliminations caused by metal salts, while the simpler olefines produced with the M—C—C$^+$ (I) irreversible fragmentations are markedly less reactive.

Consequently, a reasonable assumption is that isotope enrichment of the aromatic ring of $PhCH_2HgCl$, acted upon by DCl, may occur via a mechanism

SCHEME 4. AROMATISATIONAL METALATION



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[*] Recent papers (summarised in [31—33]; see also [34,35]) prove that the delocalisation effect of a metal in ground or spectroscopically excited states of organometallic molecules is resonant in nature. We are dealing only with the delocalising effect on chemical reactions where it relates to generation of a vacant orbital in the β-position, vis-à-vis the metal (σ- and π-generation routes [1]).

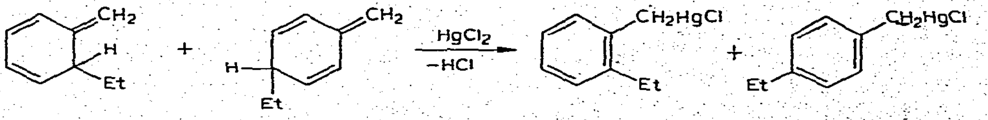
not necessarily obeying the hyperconjugation approach [3—7,9,11—16].

If the 1-methylene-6-deuteriocyclohexadiene intermediate does indeed arise in the course of the reaction of $PhCH_2HgCl$ with DCl, then this triene should be aromatised essentially by the electrophiles present in the system: deuterium chloride and, and this is the crucial point, mercuric chloride. The latter reaction should lead just to the labelled $PhCH_2HgCl$ (Scheme 4).

The main feature of the mechanism is that metal—carbon bond conservation in the course of the reaction is, however apparent, an illusion. In reality, the reaction may comprise two steps, with the C—Hg bond decomposition occurring at the first step and C—Hg bond formation in the course of the parallel retro process, aromatisational mercuration. This suggests that both the products arising from $PhCH_2HgCl$ and the acid, *α*-*o*-dideuteriotoluene and *o*-deuteriobenzylmercuric chloride, have the same precursor, the tautomeric arene. Now, it is clear why hydrogen/deuterium replacement in benzyl organometallics is always accompanied by demetalation leading to toluene ([3—15], cf. also [20]). Both courses reflect the ability of the tautomeric arenes to enter into competing electrophilic aromatisations.

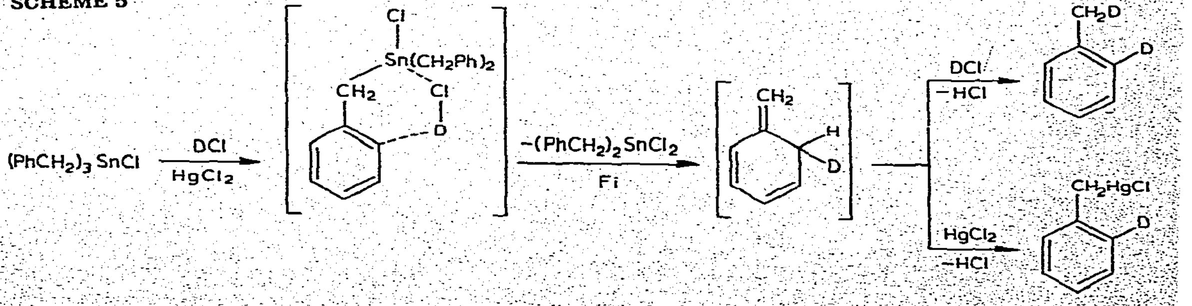
To solve the problem stated, various stereochemical and kinetic methods may be proposed. One of these may make advantage of the use of optically active compounds. The hyperconjugation stabilisation (Scheme 2) should lead to retention of configurations at the chiral metal and the carbon to which it is bonded, whereas the fragmentation pattern dictates that racemisation should occur at both centres. On the other hand, there are two different ways to test the mechanism of Scheme 4, implemented earlier by us. The respective data may be laid down as follows:

(*i*). To prove that the tautomeric arenes react with mercuric chloride, we carried out reactions of the trienes (II) and (III) with $HgCl_2$ and showed that the respective benzylmercuric chlorides were formed [1].



(*ii*). To verify that the tautomeric arenes react with salts of "soft" metals, even in strongly acidic media, we employed mercuric chloride as an electrophilic trap for 1-methylene-6-deuteriocyclohexadiene-2,4 formed intermediately in the electrophilic fragmentation course [2,36] (Scheme 5). This paper will provide a new experimental verification of this hypothesis.

SCHEME 5



2. *Deuterio-demetalation of $PhCH_2HgCl$ in the presence of mercuric chloride additive*

We assumed that valuable information on the mechanism in question could be obtained by studying the effect of metal salts on the toluene formation rate and on the deuterium content of the ring of the organometallic compound reacting with DCl.

We believed that a technique such as a pre-set increase of the $HgCl_2$ concentration in the system should not affect the mechanism since the acid cleavage of $PhCH_2HgCl$ generates necessarily $HgCl_2$ the amount of which increases with time.

Earlier it was shown that 1-methylene-6-deuteriocyclohexadiene-2,4, formed in the course of $(PhCH_2)_3SnCl$ fragmentation caused by DCl, reacts with an $HgCl_2$ additive to give $o\text{-D—}C_6H_4CH_2HgCl$ even in strongly acidic media [2]. A natural assumption is that the olefine generated by the $PhCH_2HgCl/DCl$ fragmentation could not behave otherwise. If this is so, the rationalisation of the role played by mercuric chloride in this process may allow us to distinguish between the two isotope enrichment mechanisms discussed (Scheme 2, hydrogen/deuterium replacement; Scheme 4, aromatisational metalation).

If the mechanism of Scheme 4 essentially contributes to the isotope enrichment, the increase in the $HgCl_2$ concentration should favour the $HgCl_2$-induced electrophilic aromatisation of 1-methylene-6-deuteriocyclohexadiene-2,4. Thus, the yield of the demetallation product (toluene) will be reduced and the deuterium content in the $PhCH_2HgCl$ ring augmented, when compared with the acid cleavage carried out under the conditions that involve no $HgCl_2$ additive. On the other hand, if only the σ-complex (Scheme 2) is responsible for isotope enrichment, the mercuric chloride should not affect deuterium accumulation in the aromatic ring of benzylmercuric chloride.

Figure 1 presents experimental curves describing the toluene accumulation in reactions of $PhCH_2HgCl$ with DCl in the absence (Curve I) and in the presence (Curve II) of the $HgCl_2$ additive. The reactions were studied by analysing the mixtures for toluene by quantitative GLC techniques. The curves obtained show unambiguously that $HgCl_2$ shows the formation of toluene.

To find how efficient the mercuric chloride is at altering the deuterium content in $PhCH_2HgCl$, we made the respective reactions on a preparative scale, isolated $D—C_6H_4CH_2HgCl$ and found the deuterium content of the compound. The conditions and the results are summarised in Table 1. Indeed, in all cases the deuterium content is significantly higher than in the reaction carried out in

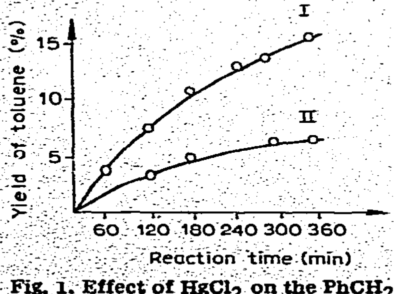


Fig. 1. Effect of $HgCl_2$ on the $PhCH_2HgCl$ deuterio-demetalation rate in dioxan at 120°C. Curve I, $[PhCH_2HgCl]_0/[DCl]_0$ 0.1/0.2; Curve II, $[PhCH_2HgCl]_0/[DCl]_0/[HgCl_2]_0$ 0.1/0.2/0.5.

TABLE 1

EFFECT OF $HgCl_2$ ON DEUTERIC-DEMETALATION AND ISOTOPE EXCHANGE IN THE REACTION OF $PhCH_2HgCl$ WITH DCl IN DIOXAN AT 120°C

Run no.	Concentration (mol/l)			Reaction time (min)	Toluene yield (%) [a,b]	Deuterium content in $DC_6H_4CH_2HgCl$ (at. %) [c,d]
	$PhCH_2HgCl$	$HgCl_2$	DCl			
1 [e]	0.25	0.00	2.50	37	50	1.71
2	0.25	1.00	2.50	37	38	13.36
3	0.25	0.50	0.50	90	6	3.13
4	0.25	1.00	1.00	90	23	9.20

[a] Found by a quantitative GCL technique. [b] The absence of isotopic exchange in toluene has been proved. [c] Found by a deuterio-analysis technique [37]. [d] The *ortho*-D-isomer, as found by IR techniques (ν-(C—dD) cm^{-1}, [11]). [e] From ref. 3.

the absence of the $HgCl_2$ additive (Table 1, Run 1) *. The experimental evidence obtained demonstrates that the isotope enrichment rate depends on the concentration of mercuric chloride formed in the course of acid cleavage.

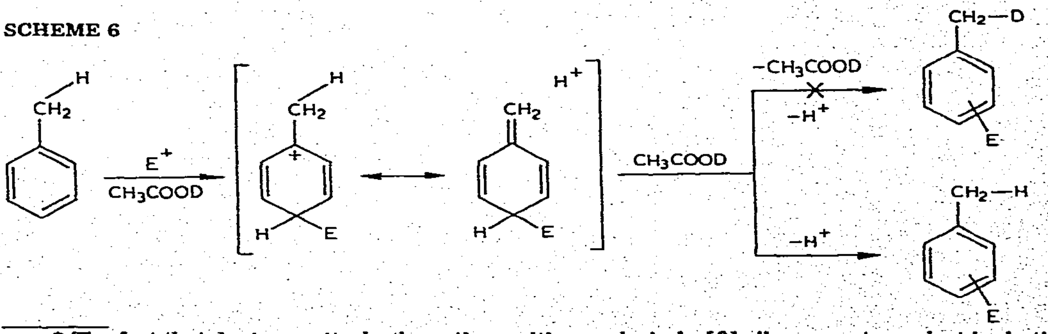
Let us now take up again the hyperconjugation conception that both demetalation, which leads to tautomeric toluene, and isotope enrichment, which leads to the deuteriated organometallics, proceed via the same intermediate species, the σ-complex [3—6,9]. The results obtained here, together with other data [2,3], suggest that this representation may be discorded. Both directions of the reaction are in good accord with the fragmentation pattern (Scheme 4) involving the *exo*-methylenecyclohexadien structure as the intermediate.

Accordingly, if we use our technique modified so as to replace $HgCl_2$ with an appropriate nucleophile, capable of binding mercuric chloride to a complex of low electrophilicity, the secondary aromatisational metalation may be suppressed considerably. We are preparing to make an investigation of this aspect.

Conclusion

The elimination nature of the C—H β-effect, stabilising the adjacent carbocation spearhead (the Nathan-Baker effect [17,18]), was first proposed by Sir

SCHEME 6



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* The fact that deuteron attacks the *ortho* position exclusively [3] allows one to neglect ionisation of DCl, under the action of the excess of mercuric chloride:
$D—Cl + HgCl_2 \rightleftharpoons D^+ HgCl_3^-$.
The ionisation would have led to a contribution from *para* attack and altered the ring protonation mechanism at the first, fragmentation, step (Fi, [1]) of the process.

Robert Robinson in 1936 [38]. This hypothesis was later dealt with in a study of the Nathan—Baker effect in isotopically labelled solvents [39,40] (Scheme 6). However, no isotope enrichment of the methyl group has ever been found, so the assumption that the Nathan—Baker effect is due to an elimination followed by proton-induced aromatisation of the kinetically independent tautomeric arene intermediate, may be, thus far, ruled out.

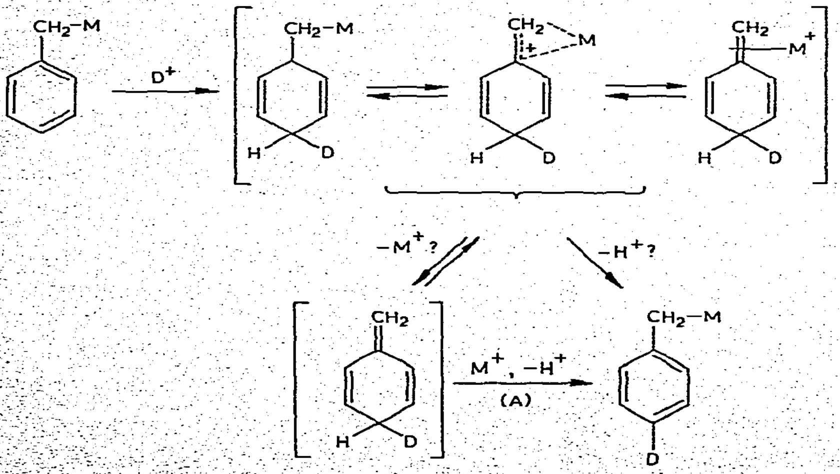
The picture is not so clear for metal—carbon bonds. Olah and Clifford [41] have found evidence in favour of the argument that non-vertical stabilisation in β-metalated carbocations is more significant than hyperconjugation. In reply, however, Traylor and Eaton [42] have provided new arguments in favour of their concept.

The present study may have shown that benzyl organometallics in their reactions with electrophiles are very appropriate models for resolving the problem in question. Indeed, using these models the crucial point of the controversy [41,42] may be reduced essentially to the questions, "*are the metal—carbon* bonds broken in the course of the reaction" and "what is the molecularity of the respective electrophilic fragmentations?"

Collating the data [19,40] with results from this paper seems to suggest that the carbon—metal β-effect on the adjacent cation spearhead differs from the C—H stabilisation effect, in that the former is an essentially "non-vertical" process. With *ortho* attack in acid cleavage of benzyl organometallics, the "non-vertical" process may be a concerted fragmentation (Fi) which leads to kinetically independent tautomeric toluene, favoured by the formation of the six-membered transition cycle [1,2,36].

As for *para* deuteriation in the benzene ring [11—15], the isotope exchange mechanism cannot, thus far, be interpreted unambiguously and one cannot choose between the "vertical" [11,12,16,42] and "non-vertical" version of the $\sigma \rightleftharpoons \pi$ conversion type [13,29,30] (Scheme 7).

SCHEME 7. NON-VERTICAL STABILISATION OF β-METALATED CARBOCATION



Earlier we have shown that the *para*-quinoid tautomeric arenes, similarly to the *ortho* species, are able to enter into aromatisational metalation [1]. Consequently, Step A in Scheme 7 above cannot be ruled out. However, whether or not the olefines, resulting from the deuteron *para* attack are kinetically independent motieties is, a priori, not yet clear.

That is why promising results may be expected from a study of the effect of adding the respective metal salts to those reaction systems in which benzyl organometallics are subject to hydrogen exchange in the *para* position of the benzene ring [1—15].

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