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ORGANOELEMENTAL FRAGMENTATIONS

I. DIRECT AND RETRO FRAGMENTATIONS IN ORGANOMETALLIC BENZYL COMPOUNDS. AROMATISATIONAL METALLATION

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Summary

Organometallic benzyl compounds are known to react with electrophilic agents via two paths, viz., by direct substitution of the metal by the agent, and by attack of the *ortho-* and *para*-positions of the ring. The latter reaction leads to expulsion of the metal and formation of unstable triene intermediates (1-methylene-2,4-cyclohexadienes and 1-methylene-2,5-cyclohexadienes). By attributing these processes to electrophilic fragmentations (referred to as F_E) a new process may be predicted to occur, electrophilic addition of metal salts to the *exo*-methylene site of trienes of this type. This process can be regarded as the reverse of the fragmentation reaction. The F_E representation proposed here forms the basis for a new organometallic synthesis, aromatisational metallation. It is shown that interaction of 1-methylene-6-ethyl-2,4-cyclohexadiene and 1-methylene-4-ethyl-2,5-cyclohexadiene with mercury dichloride in ether results in the formation of *o*- and *p*-ethylbenzylmercury chlorides, respectively.

Introduction

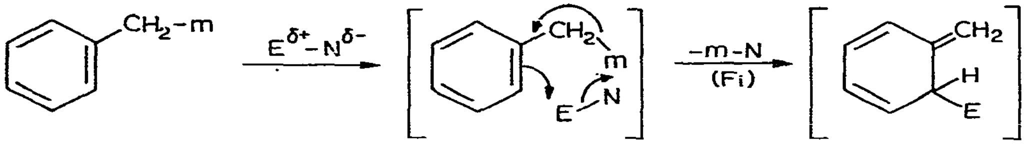
Any fragmentation may be formally related to the retro process, viz., an addition as shown below:

$$a{-}b{-}c^{\Delta} \xrightleftharpoons[\text{addition (Ad.), retro process}]{\text{fragmentation (F), direct process}} a^{\Delta} + b = c$$

$$\Delta = +, -, \cdot$$

For simpler fragmentations in three-centre systems [1], the retro processes have either been established experimentally or are easily predictable; the present paper demonstrates that this assumption may help to analyse reactivity patterns of more complex systems, the very fragmentation reactivity of which is not sufficiently evident.

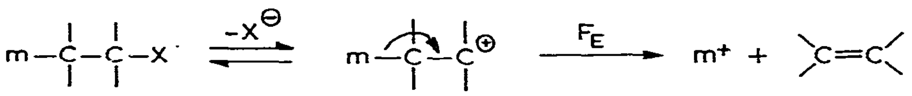
Tiffeneau and Delange [2] were the first to observe an electrophilic attack on the benzene ring in organometallic benzyl compounds. We believe that processes of this kind may also be described in terms of a fragmentation mechanism (referred to as F), and make the assumption that when exclusively *ortho*-attacks are involved, these processes are concerted fragmentations.



m = MgCl [2], ZnCl [3], HgCl [4], $B(CH_2Ph)_2$ [5], $SnCl(CH_2Ph)_2$ [6].

These reactions resemble the organometallic β-decompositions [7-9], which can be considered as fragmentations on the basis of the work of Grob and Schiess [1].

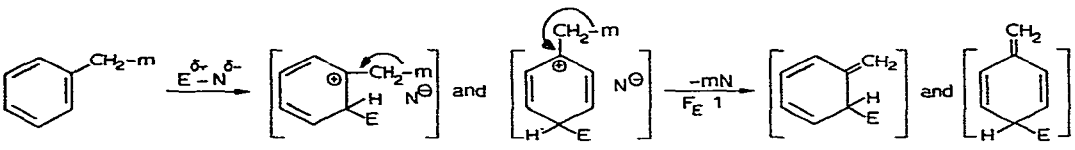
σ-route to vacant p_π-orbital



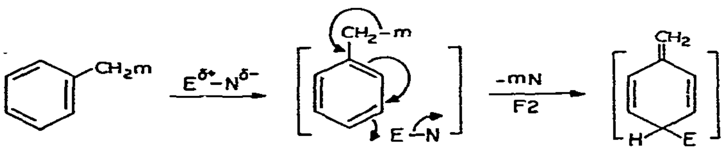
m = i-RHg, R_3Si, R_3Sn, and other groups [7-9]

The only, though significant, difference is that the organometallic benzyl compounds are subject to π-generation (according to the Winstein [10] notation) of the vacant p_π orbital β-positioned with respect to the metal. An electrophile that enters the ring at the *ortho*- or *para*-position [2-6,11] breaks the aromatic π-system, and the subsequent elimination resulting in fission of the metal—carbon bond governs the fragmentation molecularity by whether it is, or is not, concerted with the electrophilic attack on the ring.

π-route to vacant p_π-orbital



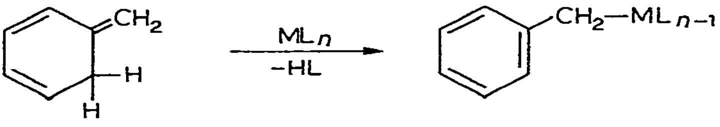
monomolecular electrophilic fragmentation



bimolecular electrophilic fragmentation

The mechanistic assignments proposed here* may be verified by finding a retro process for the reactions written above.

The *direct* process is characterised by the electrophile attack expelling the metal and generating an unsaturated hydrocarbon of the "tautomeric arene" type (the term proposed by Shorygin [13]). The *retro* process should consist in the metal salt adding to the methylene site of a triene of this type, forcing the proton out, and forming an organometallic benzyl compound.

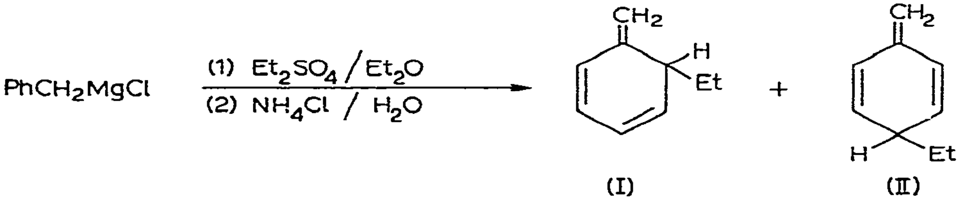


These processes, the reverse of fragmentations, may be called aromatisational metallation of the tautomeric arenes.

The present paper presents an example of the aromatisational metallation reaction which is promising from the point of view of organometallic syntheses in the benzyl series.

Aromatisational mercuration of tautomeric *o*- and *p*-ethyltoluenes

We have chosen as a model the reaction of mercury salts with tautomeric *o*- and *p*-ethyltoluenes [1-methylene-6-ethyl-2,4-cyclohexadiene (I) and 1-methylene-4-ethyl-2,5-cyclohexadiene (II)]. Benkeser et al. [14] have shown that a mixture of I and II ratio 3 : 1 can be synthesised from $PhCH_2MgCl$ and diethyl sulphate in ether, followed by treating the reaction mixture with saturated aqueous NH_4Cl.



(I) (II)

We have found that a dilute solution of mercuric chloride in ether reacts exothermally with the mixture of trienes (I and II). Evolution of HCl is observ-

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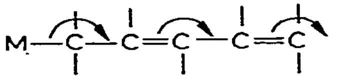
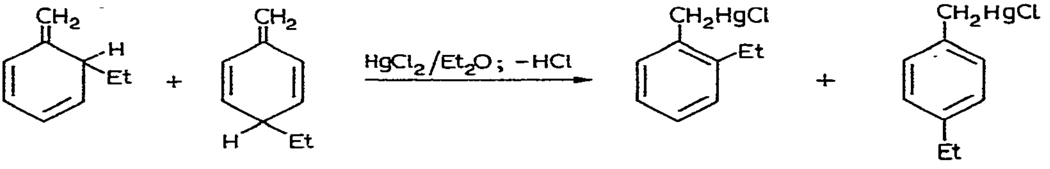
* We believe that fragmentation mechanisms [1] are quite widespread in compounds involving carbon—metal and element—metal bonds. The phenomena discussed above may be visualised in terms of Nesmeyanov's concept of reaction site transfer across the conjugated system [7].



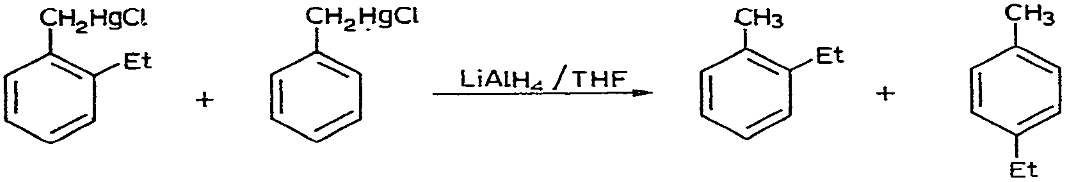
To-day, the best notation for reactions of this type is provided by the symbol S'_E where the prime refers to the allylic rearrangement [12]. We prefer Grob's fragmentation pattern [1] because this emphasises that elimination rather than substitution plays the significant role in carbon—metal bond fissions.

ed and a mixture of *o*- and *p*-ethylbenzylmercury chlorides, (III) and (IV), is formed in high yield*.



(I) (II) (III) (IV)

The resulting mixture, identified as Et-$C_6H_4CH_2HgCl$ by elemental analysis and PMR spectroscopy, was reduced with $LiAlH_4$ in tetrahydrofuran (THF) in order to find the ratio of the isomers. Gas—liquid chromatographic (GLC) separation of the expected *o*- and *p*-ethyltoluenes was tried out beforehand. The reduced reaction mixture led to a ratio of 5/1 for the hydrocarbons.



The mixture of III and IV was separated and the predominant *o*-ethylbenzylmercury chloride (III) was obtained in the pure state (m.p. 92°C). The structure was verified by elemental analysis, PMR and mass spectrometry, as well as formation of pure *o*-ethyltoluene (GLC) on reduction with $LiAlH_4$.

Discussion

The arômatisational metallation of tautomeric arenes is, in general, a two-step process. The two steps, C—metal bond formation and C—H bond decomposition, both being addition—elimination reactions, may or may not be concerted processes. The assumption of a concerted process is most natural for the

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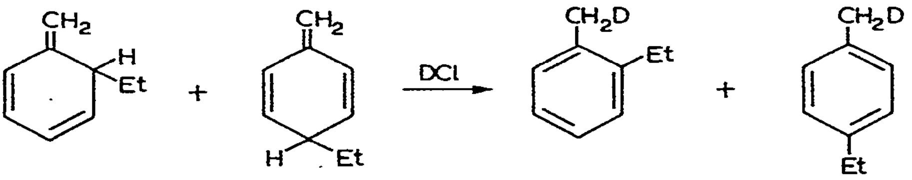
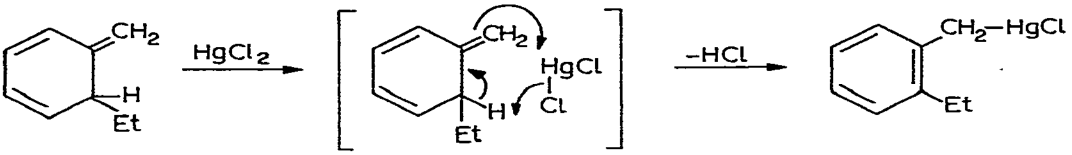
* The reaction mixture was titrated before the mercuric chloride was added and the absence of *o*- or *p*-ethylbenzylmagnesium chloride [14] was proved unambiguously. The organomagnesials could have been responsible for the formation of the organomercurials III and IV. Benkeser used an isotope technique to establish the structures of the trienes I and II. When aromatised by DCl in D_2O the compounds gave *o*- and *p*-ethyltoluenes deuteriated in the methyl group.

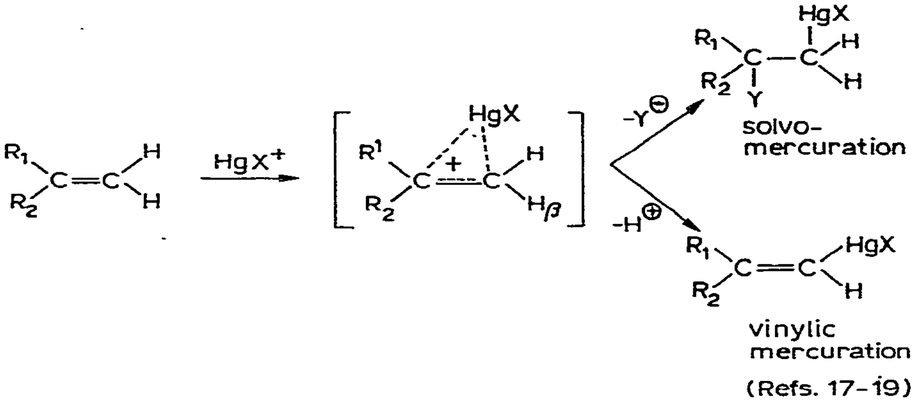


The aromatisational metallation described in this paper may serve as a method to verify unsaturated structures of this type.

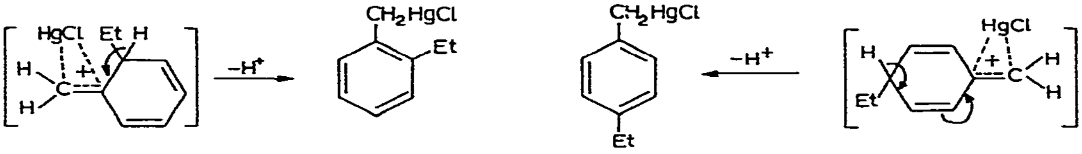
ortho-tautomeric triene, where formation of a six-membered cyclic transition state of the push—pull type may play a part.



On the other hand, the non-concerted process cannot be ruled out, since present-day theory of addition of mercury salts to unsaturated compounds asserts that so-called unsymmetrical mercurinium ions may form at the first step. The latter compounds are unstable intermediates whose existence has been proved in some special cases [15]. They are known to be stabilized via two paths, addition of a nucleophile or elimination of the β-hydrogen resulting in an unsaturated organomercurial [16].



We believe that the stabilisation via aromatisational mercuration, which consists in a proton being eliminated from position 6 or 4 of the quinoid system, is based on the fact that thereby the system may easily regain its stable, aromatic state*.



Aromatisational metallation as concept may be related to those unsaturated compounds whose structures are compatible with facile aromatisation**. In the first place, the compounds under discussion are those unsaturated species whose

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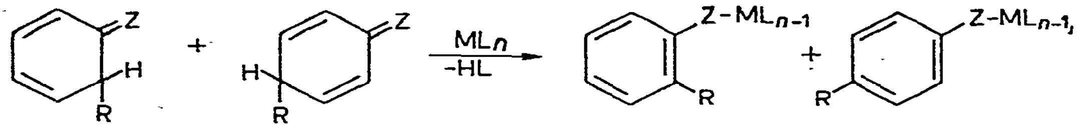
* *exo*-Methylene derivatives of polyalkylated [20] or condensed [21] arenes have been studied. In reactions of these compounds with metal salts, vinylic mercuration is as probable as is aromatisational metallation. The latter reaction should lead to decomposition of the stronger carbon—carbon bond.

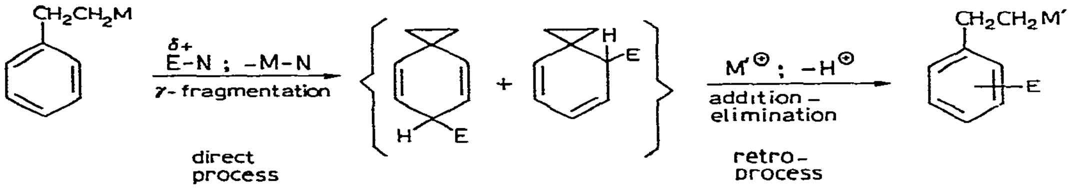
** We are studying reactions of metal salts with benzyne or norcaradiene systems.

"tautomeric" relation with their aromatic isomers results from reversible or irreversible prototropism.



$Z = O, S, NR, CR_2$

Also, reactions of this type may occur in the case of unsaturated compounds containing small rings. For instance, the demetallation observed [22] when β-(4-pyridyl)-ethylmagnesium chloride is treated with ethyl chlorocarbonate may, in our opinion, be a pronounced γ-fragmentation. *Homobenzyl* models of this type [22] may be processed through the direct/retro pattern introduced in this paper for organometallic *benzyl* compounds, in order to predict the respective retro process, in other words aromatisational metallation brought about by the action of "soft" metal salts on unsaturated spiran systems containing three-membered rings. In general, the process should lead to a homobenzyl organometallic compound.



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