

## ORGANO-ELEMENT TRANSFORMATIONS OF SEMIQUINOID COMPOUNDS

V A NIKANOROV, V I ROZENBERG and O A REUTOV

*Institute of Organo-element Compounds, Academy of Sciences of USSR,  
Moscow, USSR*

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This lecture is devoted to the organometallic chemistry of semiquinoid compounds. Investigation on these compounds were started twelve years ago at the Institute of Organo-element Compounds and at the Moscow University. The term "semiquinoid" refers to the unification and systematization of large class of organic ligands with three typical structural fragments (Fig. 1) : the exocyclic  $\pi$ -bond, the endocyclic diene  $\pi$ -system of the six-membered ring, and the saturated geminal centre.

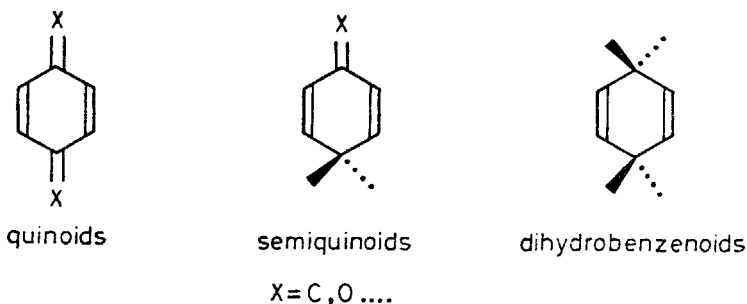


FIG 1

The semiquinoid compounds occupy an intermediate position between classical quinoid and dihydrobenzenoid  $\pi$ -systems. Although the organometallic chemistry of the two latter ligand types for a long time was an object of intensive research, the organometallic chemistry of semiquinoid compounds had been practically untouched before our efforts.<sup>1</sup>

The only known organometallic process, where semiquinoid compounds has been involved, is the reaction of benzylic organometallic compounds with electrophilic reagents.

Benzyl derivatives of transition or non-transition elements differ essentially from other organometallic systems. Indeed, their reactions with electrophiles

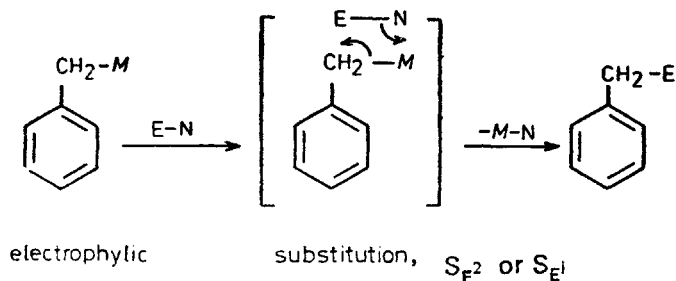


FIG 2

can proceed *via* two routes.<sup>2</sup> The usual route is the substitution at the metal-carbon sigma-bond (Fig. 2); the second, uncommon route is an attack on the *ortho*- or *para*-position of the benzene ring, resulting in unstable semiquinoid trienes<sup>2</sup> of the exo-methylene cyclohexadiene type (Fig. 3).<sup>3</sup>

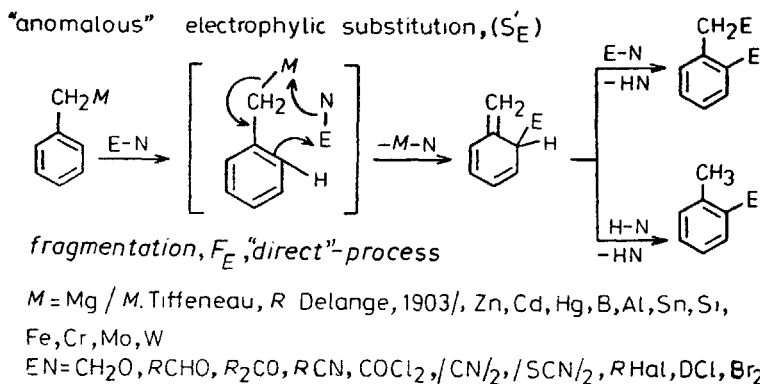


FIG 3

The trienes are then transformed to yield the final products, ring-substituted benzene compounds.<sup>2-4</sup>

Before the current investigations, the mechanism of reactions of this kind had not found its rigorous classification. A conventional term was "anomalous" electrophilic substitution. The notation was  $S'_E$ , where the prime denotes allylic rearrangement accompanying the electrophilic substitution.<sup>5</sup>

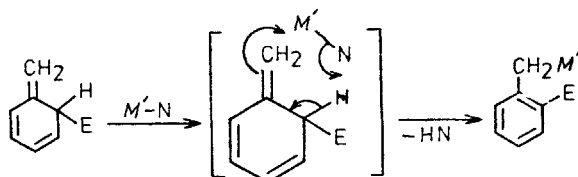
We believed, however, that a specific feature of the reactions mentioned consists in that the metal-carbon bond-cleavage occurs *via* elimination, not substitution, route. Using modern terms<sup>6</sup> we may say that fragmentation in the metal-carbon system occurs (Fig. 3). But, any elimination step may be inter-related with a reverse, or retro process, the addition.<sup>1,7</sup>

If the direct route (Fig. 3) consists of the metal elimination to produce unstable methylenecyclohexadienes, the corresponding reverse process (Fig. 4)

should involve the addition of metal salts to the exomethylene site of such trienes with proton abstraction and the formation of benzyl organometallics.

Consequently, our approach<sup>1,7</sup> allows to predict the chemical reaction, which is the reverse for the fragmentation process shown in Fig. 3.

This reaction is being called "aromatizatiional metallation"<sup>1,7</sup> (Fig. 4) and it will be the subject of the first part of our report.



"retro"-process, aromatizatiional metallation

FIG 4

Fig. 5 presents the starting model compounds chosen to study the principal possibility of the aromatizatiional metallation. These are ethyl-substituted trienes, which have been described by Benkesser as primary products of the reaction between benzylmagnesium chloride and diethylsulphate.<sup>8</sup> The authors have developed a special procedure for the purification of these trienes based on the low temperature vacuum distillation under inert atmosphere. The procedure allowed to remove dominating aromatic isomers.<sup>9</sup>

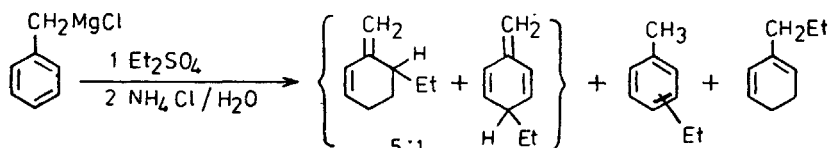


FIG 5

It has also been found that the trienes are sufficiently stable at dry ice temperatures under argon, if kept in diluted ether solutions.

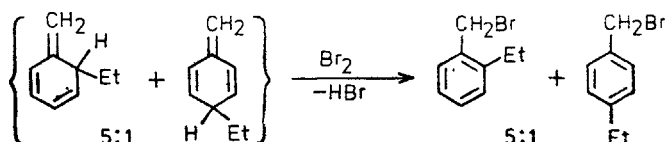


FIG 6

To determine the concentrations of unstable trienes in diluted solutions as well as their *ortho/para* ratio, the present authors have developed a method,

consisting of quantitative bromination and subsequent analysis of stable halogenated products (Fig. 6).<sup>10</sup>

Using mercury dichloride as a metallating agent, it has been established that this salt reacts exothermally with the trienes mixture. Hydrogen chloride is eliminated and, as shown in Fig. 7, a mixture of the expected *ortho*- and *para*-ethyl benzylmercury is formed. Structures of the products were verified by elemental analyses, instrumental methods and quantitative reduction to the respective ethyl toluenes.<sup>17</sup>

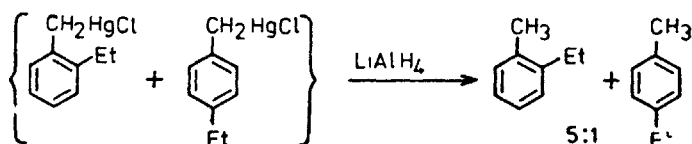
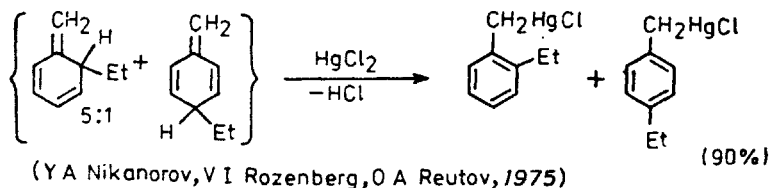


FIG 7

Other bivalent mercury salts react as readily as mercury dichloride. The reaction is independent of the nature of the anion, and the bromide or trifluoroacetate salts give the corresponding benzyl organometallics.<sup>11</sup>

The reaction discovered was promising as a general-purpose method of the synthesis of benzyl organometallic compounds.<sup>12</sup>

Actually, a high reactivity of methylenecyclohexadienes became apparent in reactions with those agents which are usually inert in metallation of simple olefines. Some examples are presented in Fig. 8.

First examples of the addition of organomercury and organo-tin compounds<sup>11,13,14</sup>, as well as of univalent gold salts<sup>15</sup> to afford the respective metal-carbon  $\sigma$ -bonds have been formed. The benzylmercury, benzyltin, or benzylgold compounds were isolated in individual forms.

The scheme shows that aromatizational metallation is always accompanied by the elimination of protic acids. The concentration of the acid increases, of course, with the reaction time. It is well known, however, that trienes of this type isomerize readily in the presence of protic acids giving the respective aromatic hydrocarbons.<sup>16-18</sup>

Nevertheless, the yields in the aromatizatiional metallation reaction are usually high.

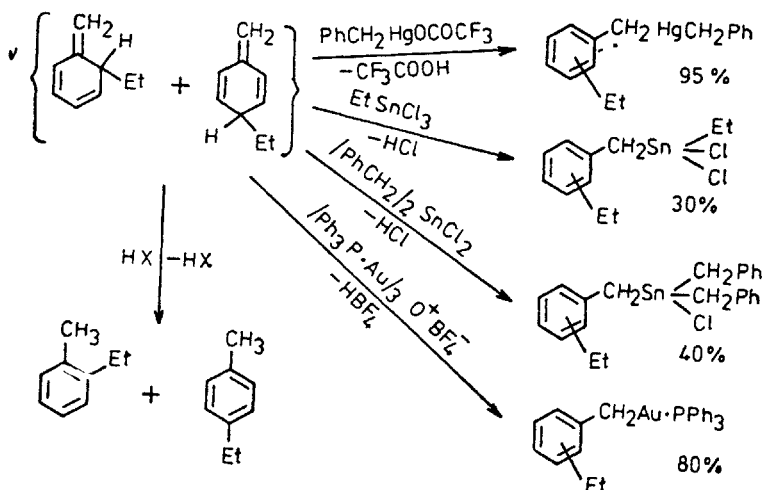


FIG 8

We believe that the driving force of our reaction is accounted for essentially by high polarizability of the semi-quinoid systems capable of being stabilised by aromatization under an electrophilic attack on the exo-methylene site of the molecule. If this is so, the fact that the aromatizatiional mercuration and the aromatizatiional auration are so facile may be explained on the basis of the Pearson principle.<sup>19,20</sup> The semi-quinoid trienes as soft bases are especially able to coordinate with soft Lewis acids such as bivalent mercury cation or univalent gold cation. Their affinity for the hard, protic acid is significantly lower.

This trend was clearly seen when the aromatizatiional mercuration was carried out in the presence of added protic acids, in other words, when mercury chloride and hydrogen chloride were competing for the trienes (Fig. 9). It appeared that even the addition of tenfold excess of the acid with respect to mercury dichloride resulted in only 15 per cent decrease in the net yield of the organometallic compounds.<sup>21</sup> The decrease was due to the *para*-isomer. The ease of mercuration of the *ortho*-isomer was practically unchanged. This is probably related to higher polarizability of the conjugated system of the *ortho*-isomer compared with the cross-conjugated system of the *para*-triene.<sup>21</sup>

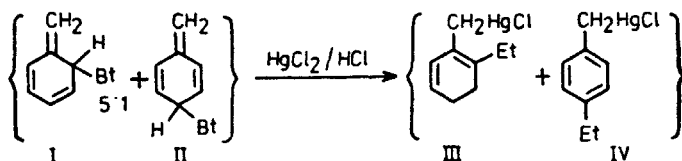


FIG 9

Changing over to such hard Lewis acid as germanium tetrachloride we were unable to germylate the trienes. This, however, was achieved, when germanium dichloride was used (Fig. 10). The compound is a metal analogue of carbene<sup>22,23</sup> and, consequently, an electrophile and a nucleophile at the same time. That

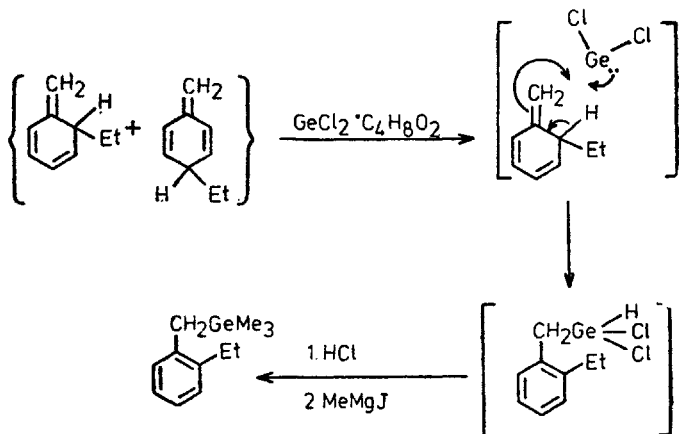


FIG 10

is why it may bind the acid resulting from the germylation of the triene and at the same time the metal is oxidized to the tetravalent state.<sup>13</sup>

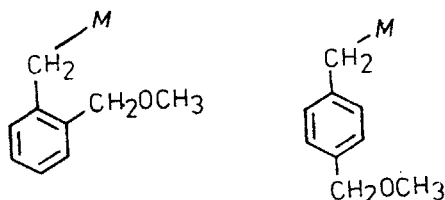
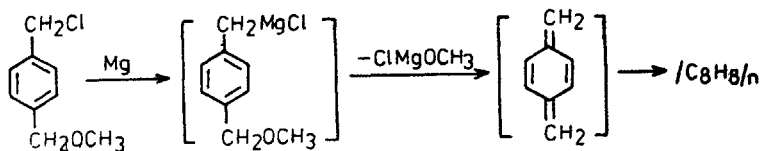


FIG 11

The aromatization metallation opened some new routes to organometallic species inaccessible *via* conventional procedures. The examples are alkoxymethyl benzyl organometallic systems shown in Fig. 11. Compounds of this kind could not be synthesized earlier<sup>24</sup> since the respective Grignard reagents decompose giving *ortho*- or *para*-xylene polymers instantaneously (Fig. 12).

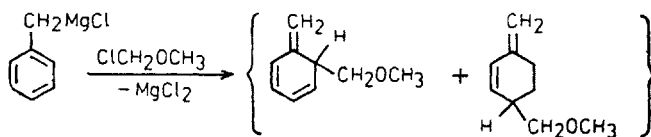


F G Mann P H C Stewart /1954/

FIG 12

One can see (Fig. 13) that the metallation of the corresponding methoxy-methyl substituted trienes obtained via Benkeser method<sup>25</sup> gave the expected organometallic compounds in high yields. Methoxymethyl substituted benzylic mercury and tin-derivatives were resolved into individual isomers and their structure was definitely established by instrumental means.<sup>26,27</sup>

We have also used this strategy to prepare a family of acyl ring-substituted benzylmercury chlorides (Fig. 14) which so far have been inaccessible.<sup>28,29</sup>



R A Benkeser, W De Talvo/1967/

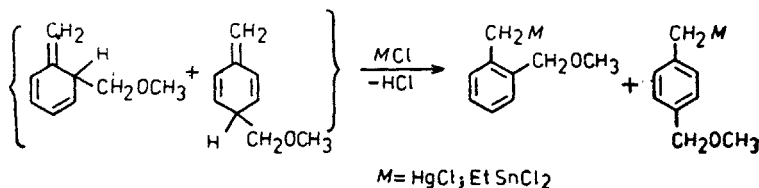


FIG 13

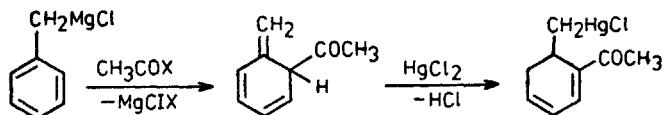


FIG 14

All the aromatization metallation reactions shown above involved the non-transition metals and afforded  $\sigma$ -bonded organometallic compounds. In Fig. 15, one can see how triene reacts with such transition metals exemplified by divalent palladium. The *ortho*-isomer, but not *para*, was the only reactive. The reaction occurs readily at the room temperature providing the  $\pi$ -benzyl derivative of divalent palladium.<sup>30</sup>

It should be mentioned that the only known straightforward approach to  $\pi$ -benzylic derivatives of this metal is the reaction with atomized palladium requiring special equipment.<sup>31</sup>

The last part of the first section of this work is concerned with mechanistic aspects. The aromatization metallation reaction helped us to unravel the mechanism of one of the most unusual organometallic processes (Fig. 16).

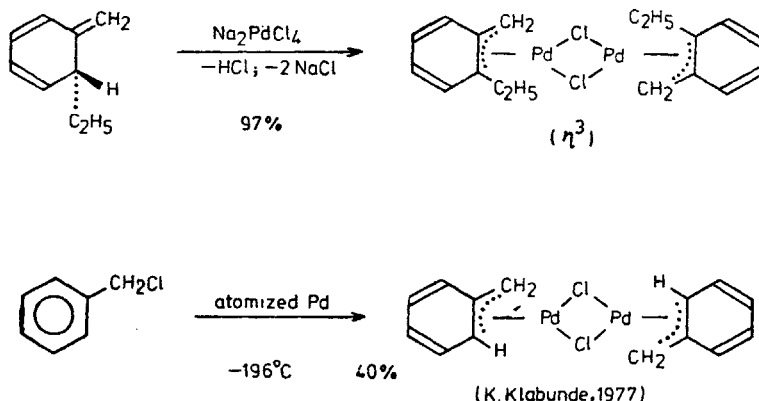


FIG 15

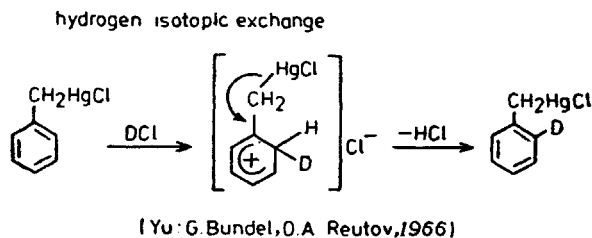


FIG 16

It was known long ago that benzyl organometallics react with isotopically labelled acids, to undergo hydrogen isotope exchange in the benzene ring. The first example—the reaction of benzyl-mercury chloride with deuterium chloride—is shown above.<sup>32</sup> A dramatic feature of this reaction is that unlike numerous reactions of organometallics with electrophiles<sup>4</sup>, the carbon-metal bond seems to remain untouched in the final product.

Before our research, the conventional explanation consisted in that the process was due to the  $\sigma$   $\pi$ -conjugation effect and, occurred *via* aromatic electrophilic substitution with conservation of the metal-carbon bond (Fig. 17).<sup>32-34</sup>

The authors paid attention, however, to the fact that isotope exchange never occurs alone, but always competes with demetallation through the intermediate methylene cyclohexadiene.

This led the authority to an assumption that it was this intermediate that could be responsible for isotope enrichment in benzylmercury product.

It was a real challenge to prove this assumption.<sup>35-36</sup> First of all we had to show the principal possibility of reaction of mercury chloride with highly unstable methylenecyclohexadiene, having two active hydrogen atoms in the geminal site. Moreover, this reaction had to take place in strongly acidic media.



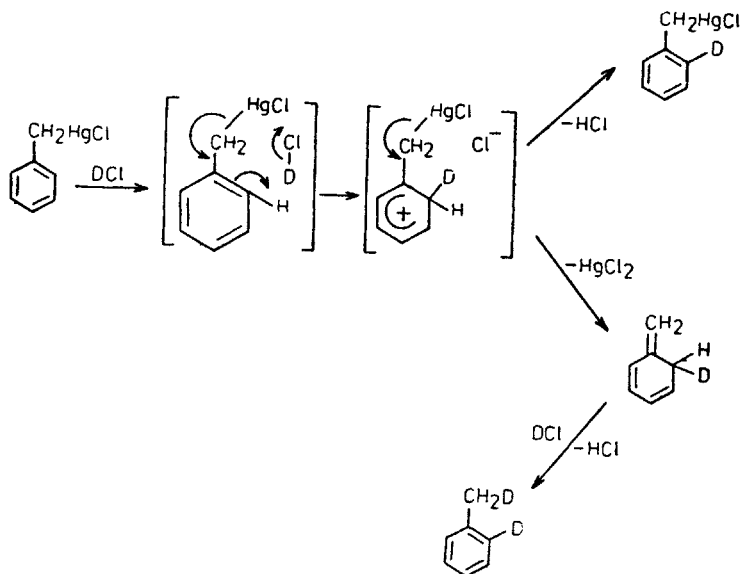


FIG 17

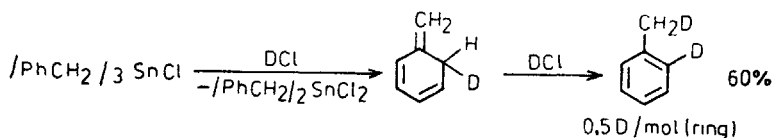


FIG 18

A tribenzylchlorostannane was chosen<sup>37</sup> for the model reaction since upon treatment with deuterium chloride it gives only deuterated toluene and this transformation proceeds as electrophilic fragmentation with the same triene intermediate (Fig. 18).

If our assumption were true, the addition of mercury dichloride to this reaction system should lead to three experimental effects :

*First* : Benzylmercury chloride should be formed in the system.

*Second* : Consequently, toluene yield should decrease.

*Third* : Benzylmercury chloride should be deuterated in the ring. Deuterium content in this product should be equal to that in toluene, since both these compounds are formed *via* a common intermediate.

The authors have really succeeded to observe all of these effects as shown in Fig. 19. So, mercury dichloride proved highly efficient as an electrophilic trap for trienes with two reactive hydrogens even in strong acid media.<sup>37</sup>

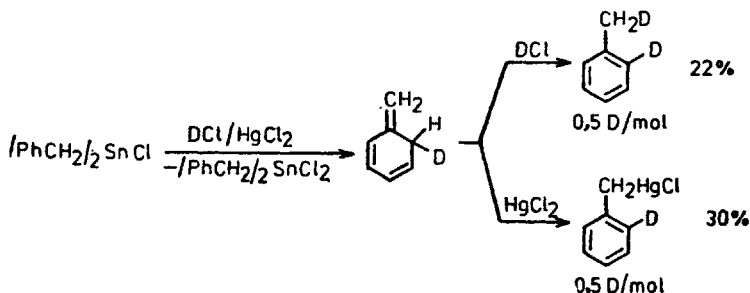


FIG 19

The decisive role of mercury dichloride in isotopic enrichment of benzylmercury chloride was proved later by kinetic and labelling experiments.<sup>35,36</sup>

Actually, the process goes via cleavage of the carbon-mercury bond at the first step (Fig. 20). This fragmentation step is followed by a recovery of the bond in the course of the retro-process—aromatization mercuration of extremely

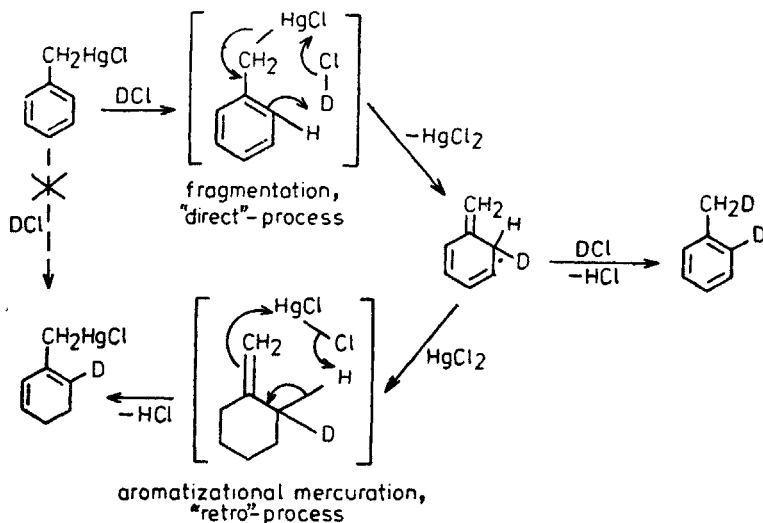


FIG 20

reactive *exo*-methylene cyclohexadiene. It means, that apparent conservation of the metal-carbon bond in the cause of the isotope enrichment is indeed an illusion.<sup>35</sup>

To sum up, the data presented here demonstrate that the aromatization-metallation reaction is not only a new method of synthesis but is also a useful model process for a study of delicate features of organo-element mechanisms in the benzyl organometallic series.

In conclusion of the first part of our report one important remark should be made.

All the reactions shown above involved semi-quinoid compounds, a specific feature of which was the presence of an active hydrogen atom in the geminal centre. Under the action of metal containing reagents, this proton is easily removed in all the cases leading only to benzyl organometallic compounds (Fig. 21).

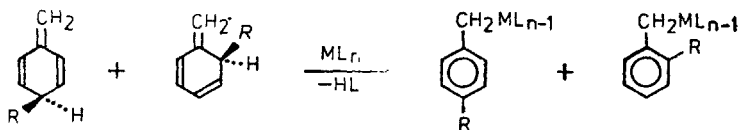


FIG 21

Changing over to semi-quinoid compounds with various groups in geminal site instead of active hydrogen could reveal new and diverse reactivity of this ligand type towards metal- and element-centered agents.

In our further work we used gem-dialkyl substituted cyclohexadienones and methylenecyclohexadienes of the *para*-semi-quinoid type (Fig. 22). Dienones are

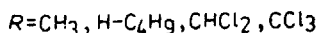
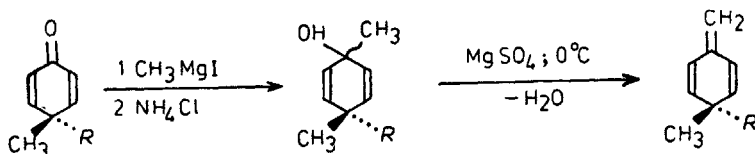


FIG 22

easily available compounds (see reviews).<sup>38,39</sup> Concerning triene—systems, it can be said that the authors have developed a very simple and reliable procedure for dehydration of the respective alcohols (Fig. 22), mild conditions of which are attained by using dilute solutions in pentane, magnesium sulphate as a neutral catalyst, low temperatures provided high yields and conservation of disubstituted trienes formed.<sup>40</sup>

We have found (Fig. 23) that the reaction of *para*-semi-quinoid trienes with phosphorus pentachloride proceeds as substitutive phosphorylation giving, after a work-up with sulphur dioxide, previously unknown exo-element substituted semi-quinoid compounds.<sup>41</sup>

The reaction proceeds regiospecifically affecting only the exo-methylene bond, independently on whether an electro-donating or electron-withdrawing substituent is located in the geminal centre.

The authors have established that the obtained phosphorylated trienes can undergo skeletal rearrangements of two different types (Fig. 24). The type of rearrangement is now strictly dependent on the nature of a geminal substituent :

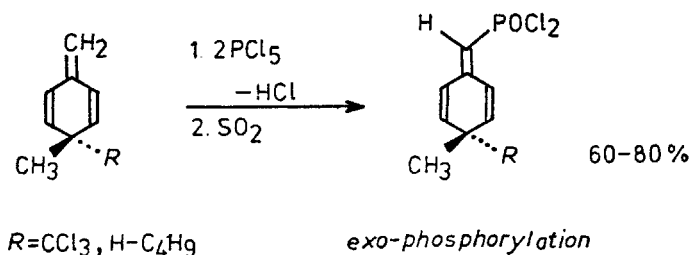


FIG 23

In particular, the  $\text{Cl}_3\text{C}$ -substituted compound undergoes 1,5-photoisomerization. The  $\text{Cl}_3\text{C}$ -group migrates from geminal site to the  $\alpha$ -position.<sup>42</sup>

On the other hand, butyl-substituted compounds easily undergo acid-catalyzed skeletal rearrangement. Such 1,2-alkyl shift from geminal centre yields both possible aromatic isomers.<sup>43</sup>

Reactivity of gem-disubstituted triene systems towards mercury salts appears to be more dependent on both the nature of the geminal substituent and the reaction conditions.

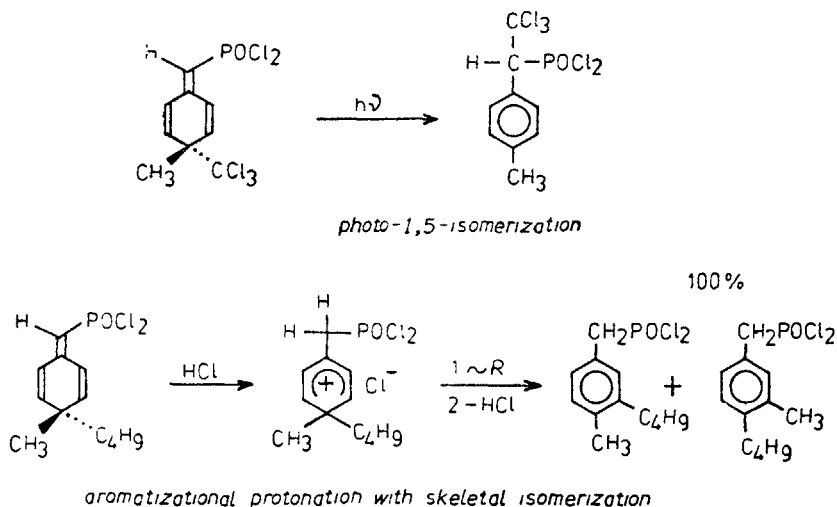


FIG 24

Three principally different pathways of mercuration have been found. If electron withdrawing groups are present in the geminal centre (Fig. 25), the reaction proceeds either as substitutional mercuration to form previously unknown exo-mono and exo-bis-metallated semiquinoid compounds or as solvomercuration. It depends on nucleophilic properties of the solvent used.<sup>44</sup>

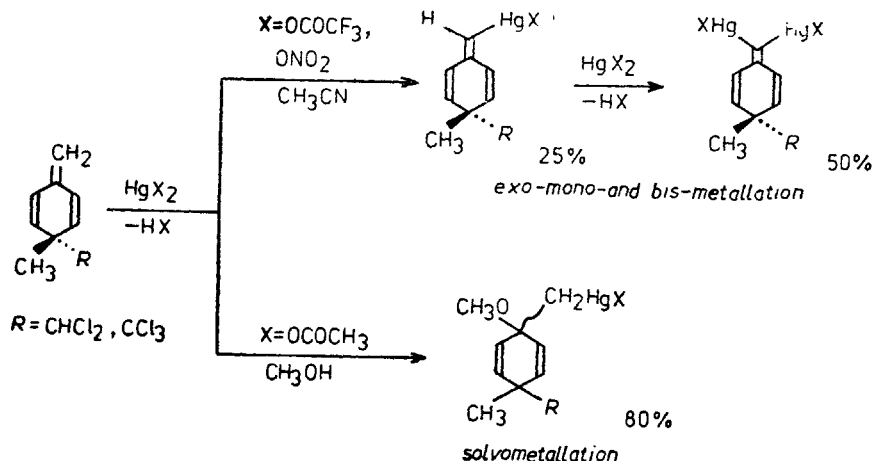
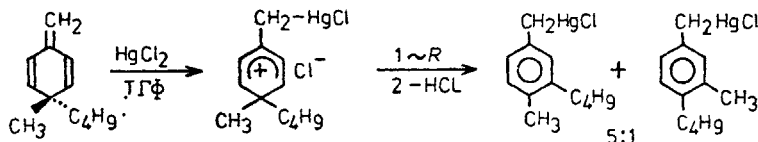


FIG 25

The presence of two electron-donating substituents in the geminal centre provides aromatizatiional metallation with skeletal isomerization (Fig 26). The process can be triggered by the action of such poor electrophile as mercury chloride.<sup>45</sup>



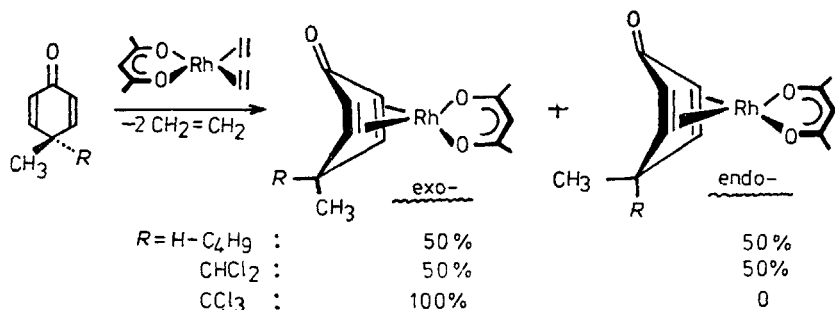
aromatizatiional metallation with skeletal isomerization

FIG 26

The above results with mercury and phosphorous have shown that disubstituted semi-quinoid molecules acting as  $\sigma$ -ligands are characterized by diverse reactivity patterns. The authors have also shown that the same is true when such molecules react as  $\pi$ -ligands in reaction with transition metal complexes (Fig. 27).

The reactions were performed with the well-known complex of univalent rhodium. The gem-disubstituted dienones react here with the formation of exo- and endo-stereoisomers in which the starting dienone behaves as a  $\eta^4$ -ligand.<sup>46</sup>

The reaction course depends crucially on the nature of the geminal substituent. In the case of bulky trichloromethyl-substituent molecule, the reaction proceeds stereospecifically and affords only exo-complexes. Stereospecificity in this case can be accounted for by assumption, that a metal atom attack from the less hindered exo-side of planar dienone molecule is much more favourable.<sup>46</sup>



unfavourable attack

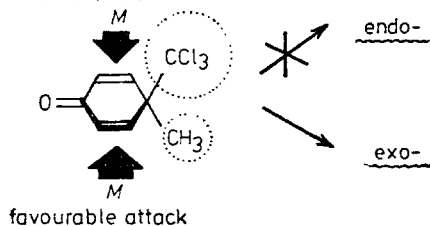


FIG 27

For the corresponding triene systems, the reaction leads to binuclear rhodium complexes in which the ligand is involved in a mixed  $\eta^2$ - $\eta^4$  coordination type (Fig. 28).

The semi-quinoid ligand is coordinated here with one rhodium atom by the  $\pi$ -diene system and with another rhodium by the exo-cyclic  $\pi$ -fragment.<sup>47,48</sup>

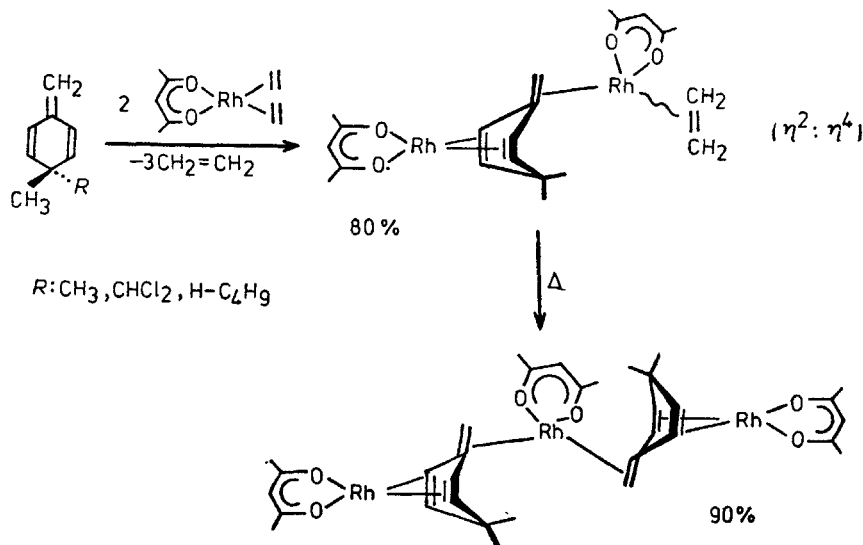


FIG 28

On heating, these compounds can undergo of symmetrization-like reaction giving trinuclear complexes. Three metal atoms are connected here with two triene ligands (Fig. 28).

Note, that in all previous cases the reaction centre of disubstituted semiquinoids was either diene or exo-cyclic  $\pi$ -systems, but not a geminal site.

Further, we will show that the geminal centre can also play a crucial role in reactivity of these compounds (Fig. 29).

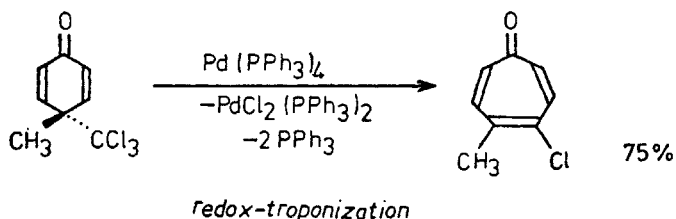


FIG 29

We have discovered that the cyclohexadienone with the geminal trichloromethyl-substituent reacts readily with zerovalent palladium to give disubstituted tropones. Taking into account evident redox nature of this rearrangement which is accompanied by palladium oxidation into the divalent state, we called this process "redox troponization".<sup>49,50</sup>

The reaction probably starts with metal insertion into the carbon-chlorine bond. Then both the metal extrusion and ring expansion in the intermediate carbene or carbanoid may take place (Fig. 30).

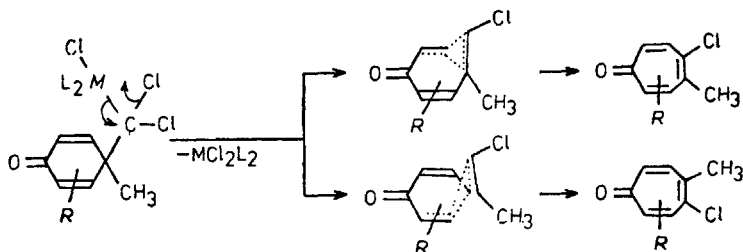


FIG 30

If ring substituents (R), either electron donating or electron withdrawing, are present, the ring expansion can occur in two ways, i.e. towards the substituent or in the opposite direction, affording a mixture of two structural isomers.

In Fig. 31 are presented some polysubstituted tropones prepared according to our procedure. Noteworthy is the fact that they all contain a chlorine atom in the ring. This is not surprising, since two chlorine atoms of  $\text{CCl}_3$ -group leave with palladium, and one remains in the expanded ring.<sup>51</sup>

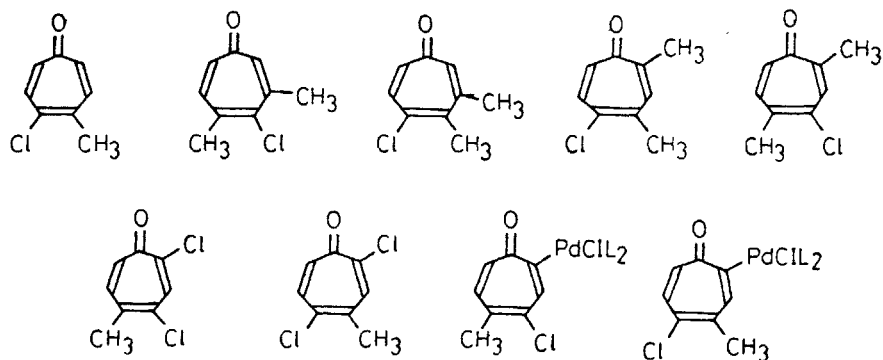


FIG 31

One may ask—is it possible to obtain in this way halogen-free tropones? Sure!

The authors only have to deal with a dihalomethyl group instead of CCl<sub>2</sub>-group in the geminal centre (Fig. 32). The reactions proceed in the same way, leading to the expected halogen-free tropones.<sup>52</sup>

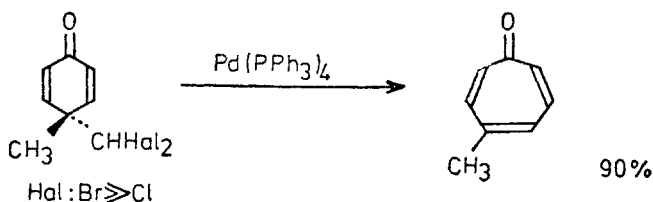


FIG 32

Our most recent investigations have been dedicated to exploring possibility of substitution of cheaper metals for rather expensive palladium in redox-troponization. Some results are presented in Fig. 33.

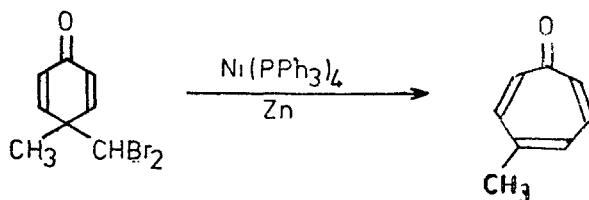


FIG 33

The authors have found that triphenylphosphine complex of zero-valent nickel readily reacts with dihalosubstituted dienones in the presence of metallic zinc Fig. 33. The reaction requires only one minute at room temperature and quantitatively yields methyltroponone.



In contrast to all the reactions discussed above one can see in Fig. 34 the first example of how redox-troponization might be applied not to *para*-semi-quinoid compounds, but rather to compounds with *ortho*-substitution pattern. The reaction appeared to be efficient for the synthesis of respective 2-substituted tropones.<sup>53</sup>

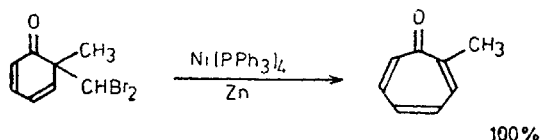


FIG 34

Along with monocyclic tropones, our reaction allows to prepare more complex tropoids, similar to some natural compounds (Fig. 35). It was planned to obtain heptafulvene here. For this purpose a novel two-ring triene ligand, having an exo-cyclic double C=C bond was prepared as a starting material.<sup>54</sup>

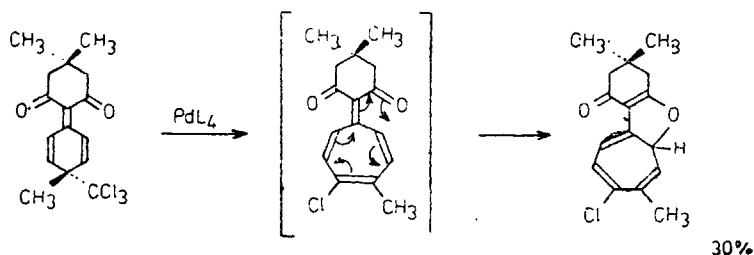


FIG 35

Indeed, treatment of this compound with zerovalent Pd did actually lead to ring expansion, but the intermediate heptafulvene compound underwent intramolecular cyclization yielding heterocyclic compound, containing 5, 6 and 7-membered rings.<sup>55</sup>

Finally, we suppose that the main result of our study is the following. Starting even from the simplest semi-quinoid compounds and using organometallic transformations one can arrive to the following structural types (Fig. 36): cyclohexadienylcarbinyls with dienesystem bonds; exo-substituted semi-quinoids with triene-system bonds; benzyl organometallics with aromatic-system bonds;  $\pi$ -complexes: mono-, bi- and trinuclear with mixed type coordinations, as well as tropones with aromatic nonbenzenoid-system bonds.

The cyclohexadienone and alkylidenecyclohexadiene chemistry has far a long time attracted considerable interest (see e.g. References 56-60) and the authors hope that the organoelement transformations studied by us will allow to get more deeper insight into the nature and chemical peculiarities of this important class of compounds.

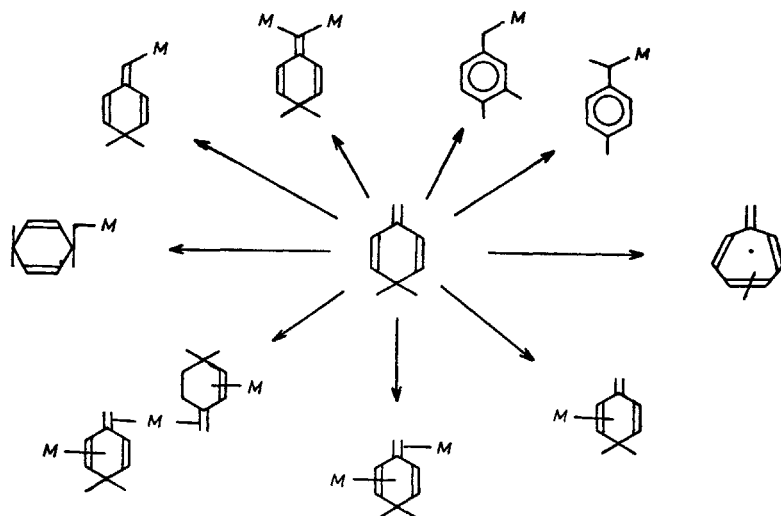


FIG 36

## CONCLUSION AND ACKNOWLEDGEMENT

In conclusion the authors would like to stress, that all the compounds shown here were isolated and fully characterized by instrumental methods. Gratitude is expressed to the authors' co-workers, Professor V I Bakhmutov, Dr M V Galakhov, Dr D V Zagorevsky, Professor Yu S Nekrasov, Dr A I Yanovsky and Professor Yu T Struchkov.

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