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DIRECT AND RETRO PROCESSES OF ORGANOELEMENTAL FRAGMENTATION

V *. AROMATISATIONAL METALLATION AS A METHOD FOR THE SYNTHESIS OF MERCURY, TIN AND GERMANIUM BENZYL DERIVATIVES **

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Summary

Aromatisational mercuration, stannylation and germylenation of 1-methylene-6-ethylcyclohexadiene-2,4 and 1-methylene-4-ethylcyclohexadiene-2,5 with several organic and inorganic mercury(II), tin(IV) and germanium(II) derivatives were studied. Interaction of the trienes with a half equivalent of $\text{Hg}(\text{OCOCF}_3)_2$ gave *o*- and *p*-di(ethylbenzyl)mercury. The reaction proceeded in two steps: at first aromatisational mercuration of methylenedihydrobenzene takes place with formation of intermediate $\text{EtC}_6\text{H}_4\text{CH}_2\text{HgOCOCF}_3$ which then reacted with a second equivalent of triene. The second step of the process was demonstrated by the reaction of trienes with $\text{C}_6\text{H}_5\text{CH}_2\text{HgOCOCF}_3$ which afforded *o*- and *p*-ethyl dibenzylmercury. The first example of addition of organomercury chloride to a carbon-carbon double bond was observed in the interaction of the trienes with $\text{C}_6\text{H}_5\text{CH}_2\text{HgCl}$ resulting in the formation of $\text{EtC}_6\text{H}_4\text{CH}_2\text{HgCl}$ and ethyldibenzylmercury. Addition of R_2SnCl_2 and R_3SnCl to the double bond was also observed in the aromatisational stannylation of 6-ethylsubstituted methylenedihydrobenzene with EtSnCl_3 and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SnCl}_2$ which gave ethyl(*o*-ethylbenzyl)dichlorostannane and dibenzyl(*o*-ethylbenzyl)chlorostannane, respectively, in high yield. Exclusive *ortho*-attack was also observed in aromatisational germylenation of a mixture of the trienes with $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$. This is the first example of aromatisational "redox"-metallation and, after treatment of the reaction mixture with HCl and MeMgI, results in the formation of *o*-ethylbenzyltrimethylgermane.

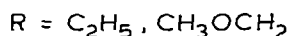
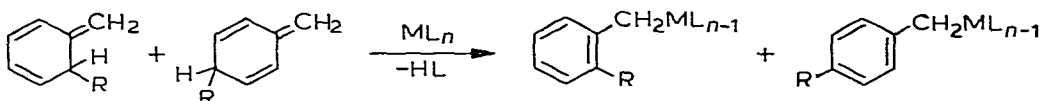
* For Part IV see ref. 1.

** Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

Introduction

Olefin metallation reactions, which play an important role in the syntheses of organo-transition metal compounds, are restricted in nontransition metal chemistry mainly to derivatives of mercury and the Group IV elements. This situation is presumably explained by the relatively low reactivity of the homologues and functional derivatives of ethylene and acetylene usually used in metallation reactions [2].

Several years ago we found that methylenedihydrobenzenes may be used as π -ligands in organometallic synthesis. They undergo aromatisation metallation with HgCl_2 [1,3-5] and $(\text{Ph}_3\text{P} \cdot \text{Au})_3\text{O}^+\text{BF}_4^-$ [6] to form mercury(II) and gold(I) benzyl derivatives:



The straightforwardness of the reaction and the exceptionally high reactivity of *exo*-methylenecyclohexadienes in electrophilic addition reactions [7] suggests that aromatisation metallation may considerably extend the group of metallating reagents usually used in the synthesis of organometallic derivatives of nontransition elements.

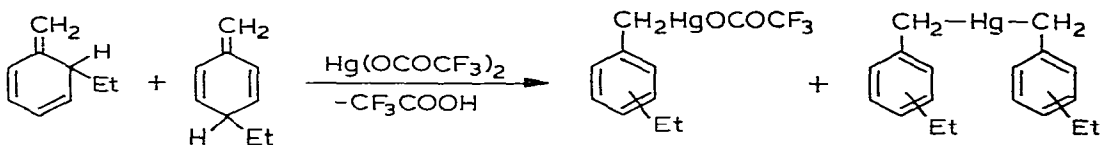
With this aim we examined the aromatisation stannylation and germylenation of methylenedihydrobenzenes in the reaction with organic and inorganic Sn^{IV} and Ge^{II} derivatives and the preparative aspects of aromatisation mercuration as a method for the synthesis of completely substituted organomercurials.

Results and discussion

1-Methylene-6-ethylcyclohexadiene-2,4 and 1-methylene-4-ethylcyclohexadiene-2,5 were selected as initial models. An ether solution of their mixture (3 : 1 ratio) was obtained following the method of Benkeser [8] and purified by low-temperature vacuum distillation (the ratio of isomers changed to 5 : 1).

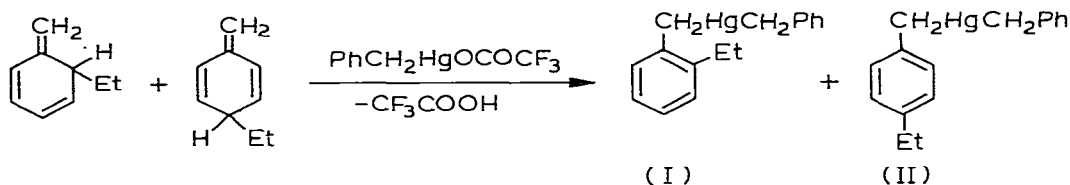
1. Aromatisation mercuration as a method for the synthesis of symmetrical and unsymmetrical completely substituted benzyl organomercurials

While studying the interaction of equimolecular amounts of mercury trifluoroacetate with a mixture of the trienes mentioned above in ether solution we found that along with the expected *o*- and *p*-ethylbenzylmercury trifluoroacetates a small amount of completely substituted benzyl organomercurials was formed:



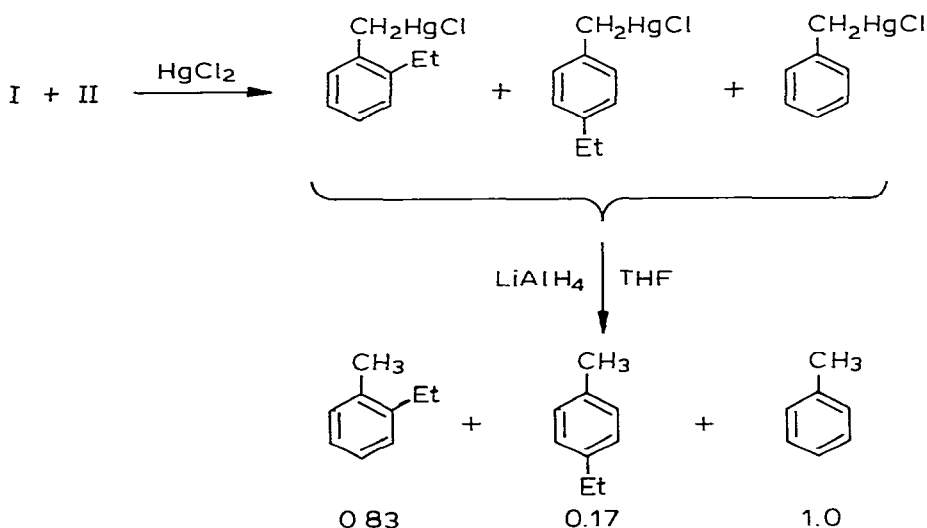
On the basis of this observation we assumed that the trienes could undergo aromatisation mercuration not only with initial $\text{Hg}(\text{OCOCF}_3)_2$, but also with the ethyl-substituted benzylmercury trifluoroacetate formed as an intermediate compound in the first step of the reaction. In order to verify this assumption we carried out the reaction of the triene mixture with a model aralkyltrifluoroacetate, namely $\text{PhCH}_2\text{HgOCOCF}_3$ [9].

Shortly after mixing equimolecular amounts of the reagents in ether solution the reaction mixture exhibited an acidic reaction and ethyl-substituted dibenzylmercury was formed (chromatographic and spectral data):



In order to determine the structure and the isomeric composition of the products we undertook dissymmetrisation of the obtained mixture of *o*- (I) and *p*- (II) isomers with an equimolecular amount of HgCl_2 in THF. PMR spectroscopy of the reaction products revealed that, as expected, a mixture of *o*- and *p*-ethylbenzylmercury chlorides and an equimolecular amount of PhCH_2HgCl had been formed (Scheme 1) from which *o*-ethylbenzylmercury chloride could be easily isolated. Reductive cleavage of the mixture of organomercurial salts by LiAlH_4 in THF with subsequent quantitative GLC analysis established the presence of three compounds, namely toluene and a mixture of *o*- and *p*-ethyltoluenes:

SCHEME 1

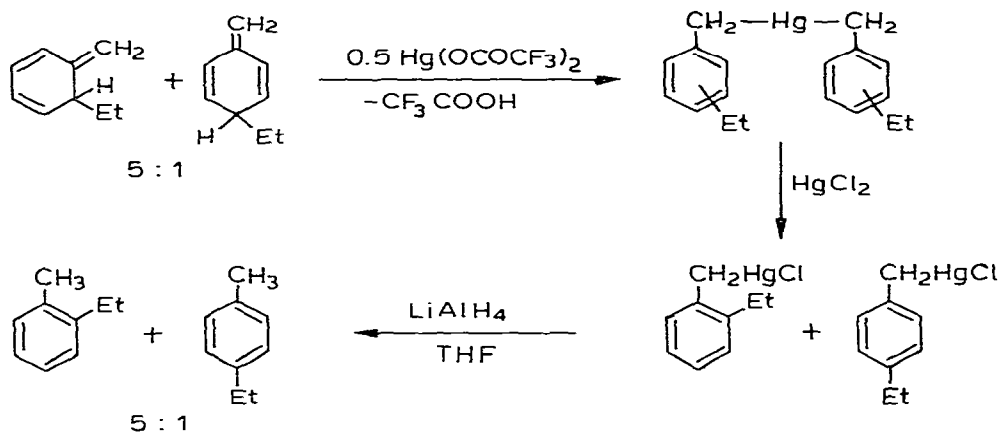


The observed ratio of the aromatic hydrocarbons (0.83/0.17/1) indicates that both isomeric methylenedihydrobenzenes interact with $\text{PhCH}_2\text{HgOCOCF}_3$ with the same ease since the isomeric composition of the organomercurials

formed precisely reproduces the initial ratio of trienes (5/1) and unambiguously confirms that the structures of compounds I and II correspond to *o*- and *p*-ethylbenzylmercury (since the ratio of toluene to the mixture of *o*- and *p*-ethyltoluenes is 1/1). These results indicate that $\text{PhCH}_2\text{HgOCOCF}_3$ may indeed attack the *exo*-methylene site of 6- and 4-substituted methylenedihydrobenzenes with elimination of CF_3COOH and formation of unsymmetrical completely substituted benzyl organomercurials.

The reaction described above is one of the few examples known of electrophilic addition of organomercury trifluoroacetates to carbon-carbon double bonds (cf. refs. 10) and may be of considerable theoretical interest as a model process for the study of hyperconjugation of the C-Hg bond [11] in connection with the mechanism of deuterium exchange in dibenzylmercury under the action of isotopically labelled acids [9,12].

The results obtained were also used to define conditions for the synthesis of symmetrical completely substituted benzyl organomercurials from mercury trifluoroacetate:

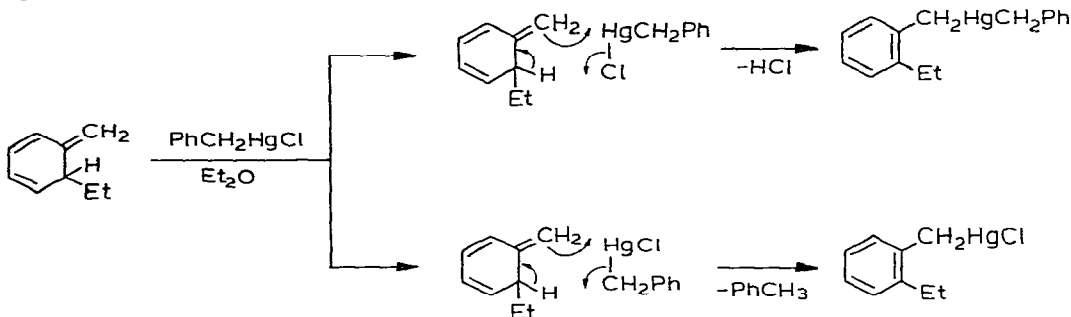


When using a 1.5-fold excess of trienes in relation to the mercurating agent the expected di(ethylbenzyl)mercury is formed in 90% yield. The reaction proceeds in two steps, namely aromatisational mercuriation of methylenedihydrobenzenes to form ethyl-substituted benzylmercury trifluoroacetates followed by aromatisational mercuriation of the latter with a second equivalent of the triene mixture. Data on the reductive cleavage, which unambiguously reproduces the isomeric composition of the initial triene mixture, indicate that both steps of the reaction are statistical processes and result in the formation of an equilibrium mixture of all three possible structural isomers, *o,o*-, *o,p*- and *p,p*-di(ethylbenzyl)mercury. This is also supported by additional splitting in the PMR spectra of the isolated organomercurials.

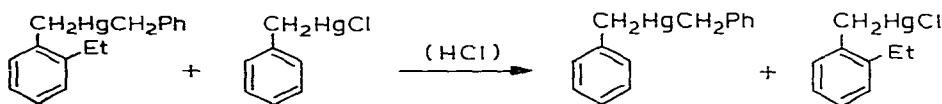
In concluding this part of the work we examined the possibility of aromatisational mercuriation of methylenedihydrobenzenes with PhCH_2HgCl . The latter is a weak electrophile, as are other organomercury chlorides, and is in general incapable of addition to the usual unsaturated compounds. In this case, however, the reaction did occur, although in low yield, and resulted in the formation of two compounds, *o*-ethylbenzylmercury chloride and ethyldibenzylmercury in 1/1 ratio. The structure of these compounds was verified by inter-

nal referencing of the PMR spectra of the mixture to isolated organomercurials.

Formation of ethyldibenzylmercury in this reaction is apparently the first example of organomercury chloride addition to a carbon-carbon double bond; formation of the accompanying organomercurial, *o*-ethylbenzylmercury chloride, possibly reflects an alternative aromatisational mercuriation route in the system studied:

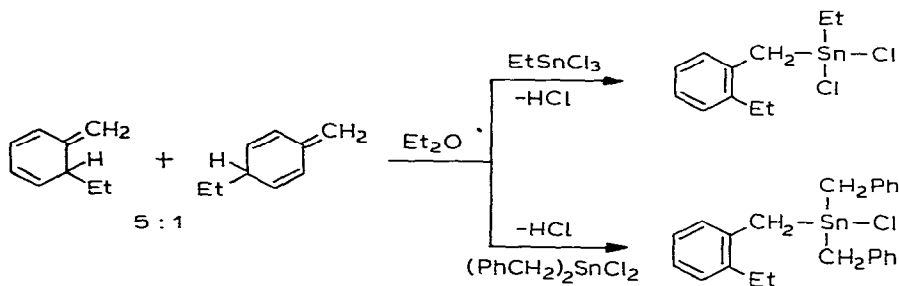


The contribution of trialkyl exchange between the ethyldibenzylmercury with the initial PhCH_2HgCl should, however, also be taken into account when explaining the formation of *o*-ethylbenzylmercury chloride. This possibility was checked in a separate experiment with *o*-ethyldibenzylmercury which revealed the formation of a small amount of *o*-ethylbenzylmercury chloride:



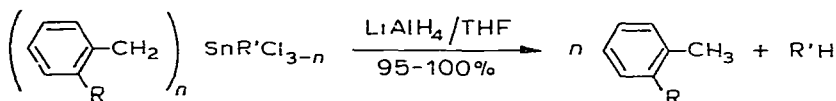
2. Aromatisational stannylation

Just as the benzylmercury chloride discussed in the preceding section, organotin chlorides are also weak electrophiles and are in general incapable of addition to the double bonds of the usual unsaturated compounds. However, on going to methylenedihydrobenzenes, possessing higher reactivity with respect to Lewis acids, an aromatisational stannylation reaction does proceed. This reaction provides a means for the direct aralkylation of organotrichloro- and diorganodichlorostannanes, yielding unsymmetrical diorganodichloro- and triorganochlorostannanes, respectively [13]:



The structure of these compounds was determined by means of elemental analysis and PMR spectroscopy. In order to determine the isomeric composition a method of reductive cleavage of the obtained organotin chlorides was

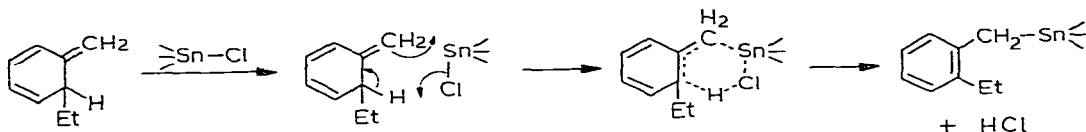
employed involving heating with LiAlH_4 in THF which resulted in quantitative rupture of the C—Sn bond:



$n = 1$ ($\text{R} = \text{R}' = \text{Et}$), 2 ($\text{R} = \text{H}$; $\text{R}' = \text{PhCH}_2$, $o\text{-EtC}_6\text{H}_4\text{CH}_2$, Cl)

The method was checked with standard $(\text{PhCH}_2)_2\text{SnCl}_2$ and $(\text{PhCH}_2)_3\text{SnCl}$.

GLC analysis revealed only the presence of *o*-ethyltoluene. This implies that, unlike aromatisational mercuration, aromatisational stannylation proceeds most readily with the *ortho*-semiquinoid form of methylenedihydrobenzene. This may be rationalised in terms of a concerted pericyclic mechanism with formation of a closed six-membered transition state incorporating six electrons in a field of six nuclei:



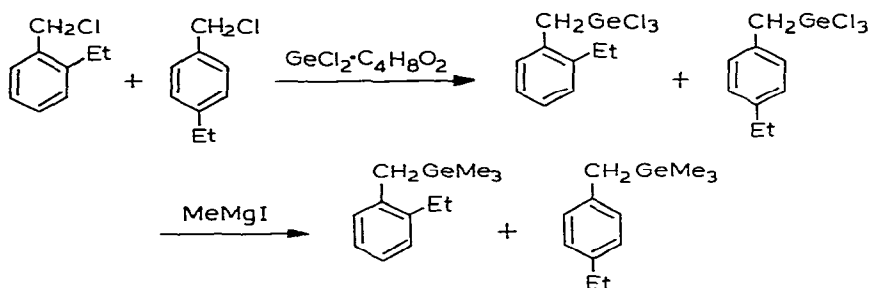
It should be noted that this procedure of preparing tin benzyl derivatives allows one to synthesize in a single step and in high yields isomerically pure organotin compounds containing several different substituents at the metal atom. Preparation of such compounds by the usual methods requires multi-stage syntheses under rigorous conditions and may be accompanied by secondary disproportionation reactions resulting in poorly separable mixtures.

3. Aromatisational germylenation

Germyleation products were not observed in the reaction of the ether solution of 6- and 4-methylenedihydrobenzenes with germanium tetrachloride, even after prolonged refluxing of the reaction mixture in THF. However, the use of dichlorogermylene dioxanate [14] as a metalating agent was considered to be more likely to yield organogermanium benzyl compounds.

Addition of the trienes to a refluxing solution of $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ in THF resulted in the formation of an organogermanium compound (as revealed by paper chromatography; yellow colouring when developed with dithizone). Then, without isolation of the intermediate compound, the reaction mixture was consecutively treated with an excess of HCl in ether and with an ether solution of MeMgI (Scheme 2). GC/MS analysis confirmed the presence of ethylbenzyltrimethylgermane in the reaction mixture.

The yield and isomeric composition of germyleation products were determined by quantitative GLC. Previously, authentic samples of the expected *o*- and *p*-ethylbenzyltrimethylgermanes had been obtained by independent syntheses (using the method described in ref. 15) and conditions for chromatographic resolution were determined:



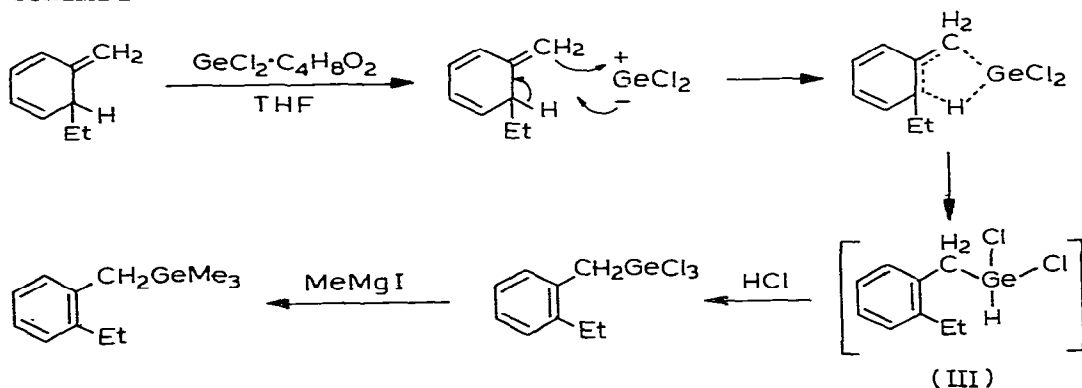
It was found that the main product of aromatisation of the triene mixture with dichlorogermylene dioxanate and of subsequent treatment with HCl and MeMgI was *o*-ethylbenzyltrimethylgermane (yield 20%; the corresponding *p*-isomer was present only in trace amounts).

In general one could expect that trichlorogermene (HGeCl_3), which might be present in $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$, was responsible for the formation of the organogermanium benzyl compound. However, in a separate experiment it was shown that the reaction of the triene mixture with authentic HGeCl_3 yields only trace amounts of *o*-ethylbenzyltrimethylgermane. Even in this reaction formation of the latter may be attributed to GeCl_2 which is present in dynamic equilibrium with HGeCl_3 [16]:



Therefore, it is the germylene chloride that is the metalating agent in aromatisation of methylenedihydrobenzenes, resulting in the formation of the organogermanium benzyl compound. The GeCl_2 molecule, being a metallic analogue of carbene [17], has at its reaction site (at a germanium atom) a vacant orbital and a lone electron pair. It therefore possesses both electrophilic and nucleophilic properties and may bound the proton eliminated during aromatisation of the triene. Since transition of the germanium atom into the tetravalent state occurs at the same time, this reaction may be considered the first example of aromatisational "redox" metallation during which reduction of the semiquinoid system is accompanied by simultaneous oxidation of the metal:

SCHEME 2



Predominant formation of the *ortho*-isomer in this reaction can be considered as evidence in favour of a concerted pericyclic mechanism via a closed transition state incorporating six electrons in a field of five nuclei. In this case, the primary reaction product should be *o*-ethylbenzyl dichlorogermane containing a Ge—H bond (III) (Scheme 2). Indeed, in one of the experiments, after carrying out aromatisational germylenation before treatment with acid we observed in the IR spectrum of the reaction mixture an absorption band of weak intensity at 2115 cm^{-1} , which seems to belong to the intermediate hydride III (according to literature data Ge—H absorption bands for alkyl dichlorogermanes should be exhibited in the 2100 cm^{-1} region [18,19]).

Experimental

PMR spectra were recorded on Varian T-60 and Varian XL-100 instruments in 10–15% CH_2Cl_2 solutions, using HMDS as external and TMS as internal standards. IR spectra (Nujol mulls) were obtained on a UR-20 spectrophotometer.

Quantitative GLC analysis of mixtures of *o*- and *p*-ethyltoluenes was carried out according to ref. 5. Quantitative GLC analysis of ethylbenzyl chloride mixtures was performed with a LKhM-8 instrument using glass columns filled with Rheoplex-40. GLC analysis of organogermanium compounds was carried out on a Tsvet-2 chromatograph with 15% Apiezone L on Chromaton N-AWDMCS. Durol was used as a reference for calibration of the reaction mixtures. GC/MS analysis was carried out with a Varian MAT-111 instrument equipped with a steel column ($l = 2.5\text{ m}$, $d = 0.4\text{ mm}$) filled with Carbowax-20M. For paper chromatography pentane was used as an eluent and dithizone as a developer.

Mixtures of 1-methylene-6-ethylcyclohexadiene-2,4 and 1-methylene-4-ethylcyclohexadiene-2,5 in ether were obtained according to Benkeser [8] and in some cases were purified by low-temperature distillation. Triene concentration (2%) and isomeric ratio (5 : 1) were determined by bromination [20]. The solvents used were purified by the usual techniques; the starting materials and chromatographic standards: *o*- and *p*- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{HgCl}$ [5], *p*- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ [21], $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SnCl}_2$ [22], $\text{C}_2\text{H}_5\text{SnCl}_3$ [23], *o*- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{CH}_3$, *p*- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{CH}_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{HgCl}$, $\text{C}_6\text{H}_5\text{CH}_2\text{HgOCOCF}_3$ and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Hg}$ were obtained by literature methods. $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ [14] and HgCl_2 were purified by recrystallization from dioxane and methanol respectively, GeCl_4 by distillation. HgGeCl_3 was obtained by "direct" synthesis and therefore contained an admixture of GeCl_4 (15%). It was established by GLC and PMR methods that the *p*- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ obtained according to ref. 21 contained an admixture of *o*- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ (5%).

Aromatisational metallation reactions were carried out under argon atmosphere.

o,o-Di(ethylbenzyl)mercury. An alkaline solution of sodium stannite prepared from 0.42 g of NaOH in 2.5 ml of H_2O and 0.17 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 2.5 ml of H_2O was added to a suspension of 0.2 g (0.56 mmol) of *o*- $\text{EtC}_6\text{H}_4\text{CH}_2\text{HgCl}$ in 0.5 ml of EtOH and 10 ml of H_2O . The reaction mixture was stirred for an hour, filtered, dried and treated with acetone. Isolation of the reaction product by addition of several drops of water to the acetone extract at -15°C gave 0.1 g (90%) *o,o*-di(ethylbenzyl)mercury, m.p. 65°C . PMR (δ , ppm): 1.45 (3H,

CH₃ triplet); 2.60 (4H, CH₂Hg, singlet, $J(^1\text{H}-^{199}\text{Hg})$ 134 Hz); 2.90 (4H, CH₂ quartet); 7.16 (8H, C₆H₄ multiplet).

o- and *p*-ethylbenzyltrichlorogermanes. 1.15 g (5 mmol) of dichlorogermylene dioxanate were added to 7.7 g (0.05 mol) of *p*- and *o*-ethylbenzyl chloride mixture. The solution was heated for 8 h at 130°C and the reaction products were then isolated by fractional distillation at 120–123°C (5 mm Hg), yield 0.53 g (36%). PMR (δ , ppm): 1.10 (3H, CH₃ triplet); 2.47 (2H, CH₂ quartet); 3.06 and 3.25 (4H, two CH₂-Ge singlets); 7.03 (4 H, C₆H₄ multiplet). According to the PMR data the substance is a mixture of *p*- and *o*-isomers, ratio 0.1/1.

o- and *p*-ethylbenzyltrimethylgermanes. 0.53 g (1.8 mmol) of ethylbenzyltrichlorogermanes obtained in the preceding experiment in 5 ml of ether were added with stirring over a period of 2 h to 25 ml of MeMgI in ether solution, obtained from 0.17 g (7×10^{-3} g-atom) of Mg and 1 g (7 mmol) of CH₃I. After boiling for 8 h the reaction mixture was treated with saturated aqueous NH₄Cl, the ether layer was removed and dried over CaCl₂. The reaction product was isolated by fractional distillation at 110–113°C (10 mmHg), yield 0.32 g (75%). PMR (δ , ppm): 0.05 (9H, CH₃-Ge singlet); 1.15 (3H, CH₃ triplet); 2.05 and 2.15 (4H, two CH₂ singlets); 7.10 (4H, C₆H₄ multiplet). According to GLC and PMR data the substance is a mixture of *o*- and *p*-isomers, ratio 0.1/1.

Aromatisational mercuration

Interaction of trienes with Hg(OCOCF₃)₂. Preparation of o- and p-di(ethylbenzyl)mercury. 0.21 g (0.5 mmol) of Hg(OCOCF₃)₂ in 10 ml of THF were added at 0°C with stirring over a period of 0.5 h to 250 ml of an ether solution (1.5 mmol) of trienes (purified by low-temperature distillation). R_f (Hg(OCOCF₃)₂) = 0.05, R_f product 0.95 (the reaction was monitored by paper chromatography). After completion of the reaction, the solvent was evaporated off and the remaining oil chromatographed in pentane on a column ($l = 5$ cm, $d = 2$ cm) filled with SiO₂ grade "Chemapol" 5/40 μ . Evaporation of the eluent and drying of the semicrystalline product under reduced pressure (2 mm Hg) over CaCl₂ and paraffin gave 0.2 g (91%) of a mixture of *o*- and *p*-isomers, m.p. 27–31°C. PMR (δ , ppm): 1.54 (3H, CH₃ multiplet); 2.66 (4H, CH₂Hg singlet, $J(^1\text{H}-^{199}\text{Hg})$ 136 Hz); 3.02 (2H, CH₂ quartet); 7.24 (8H, C₆H₄ multiplet).

Determination of the isomeric composition of o- and p-di(ethylbenzyl)mercury

1. *Dissymmetrization of di(ethylbenzyl)mercury.* 1 mmol of the organomercurials obtained in the preceding experiment in 40 ml of acetone was added dropwise to a heated solution of 0.27 g (1 mmol) of HgCl₂ in 5 ml of acetone. The mixture was refluxed for 4 h, and after termination of the reaction (determined by paper chromatography) the solvent was evaporated and the solid residue was extracted with 4 ml of abs. CHCl₃ from the unreacted HgCl₂. Evaporation of chloroform under reduced pressure gave 0.31 g (97%) of *o*- and *p*-ethylbenzylmercury chlorides, m.p. 55–60°C (mixture of isomers). PMR (CH₂Cl₂, δ , ppm): 1.58 (3H, CH₃ triplet); 3.02 (2H, CH₂ quartet); 3.45 (2H, CH₂-Hg singlet, $J(^1\text{H}-^{199}\text{Hg})$ 282 Hz); 7.28 (4H, C₆H₄ multiplet).

2. *Reductive cleavage of o- and o-ethylbenzylmercury chlorides.* 0.31 g (0.97

mmol) of the organomercurial salts in 15 ml of THF were added dropwise to a suspension of 0.1 g (3 mmol) of LiAlH_4 in 10 ml of THF and the mixture was refluxed. The reaction was monitored by paper chromatography. After completion of the reaction the excess of hydride was quenched with water, 0.019 g (0.18 mmol) of ethylbenzene was added as a chromatographic reference, the mixture was extracted with pentane (4×5 ml), the pentane solution was separated and dried over MgSO_4 . GLC analysis revealed that the reduction products were a mixture of *o*- and *p*-ethyltoluenes, ratio 5 : 1, yield 92% with respect to $\text{Hg}(\text{OCOCF}_3)_2$.

Reaction of trienes with benzylmercury trifluoroacetate. Preparation of ethyldibenzylmercury. 190 ml (3 mmol) of the triene mixture in ether were added over a period of 0.5 h to 1.21 g (3 mmol) of $\text{PhCH}_2\text{HgOCOCF}_3$ in 25 ml of ether at room temperature. Slight acidification of the reaction mixture and formation of a new organomercurial with R_f 0.98 (pentane) were observed. After completion of the reaction (determined by paper chromatography) the reaction mixture was evaporated and the oil-like residue crystallized by consecutive treatment with methanol and pentane and dried under vacuum, yield 1.15 g (93%). PMR (CH_2Cl_2 , δ , ppm): 1.5 (3H, CH_3 multiplet); 2.60 and 2.66 (4H, two $\text{CH}_2\text{-Hg}$ singlets, $J(^1\text{H-}^{199}\text{Hg})$ 136 Hz); 2.9 (2H, CH_2 quartet); 7.2 (9H, C_6H_5 and C_6H_4 multiplets).

The isomeric composition of the mixture was determined by the method described above. 1.15 g of organomercurials were dissymmetrised with an equimolar amount of HgCl_2 in acetone to yield 1.82 g (96%) of a mixture of *o*- and *p*-ethylbenzylmercury chlorides (50%) and benzylmercury chloride (50%). PMR (CH_2Cl_2 , δ , ppm): 1.58 (3H, CH_3 triplet); 3.0 (2H, CH_2 quartet), 3.46 and 3.53 (4H, two $\text{CH}_2\text{-Hg}$ singlets); 7.3 (9H, C_6H_5 and C_6H_4 multiplets). Subsequent reduction of the mixture of organomercurials with LiAlH_4 in THF gave a mixture of three aromatic hydrocarbons: *o*- and *p*-ethyltoluenes in 5/1 ratio (50%) and toluene (50%). In a separate experiment pure *o*-ethylbenzylmercury chloride was isolated from the mixture of the three organomercury chlorides by reprecipitation from CH_2Cl_2 with MeOH and collection of the first fraction of crystals formed upon cooling, yield 0.1 g, m.p. 92°C (lit. [5] 92°C). PMR (δ , ppm): 1.58 (3H, CH_3 triplet); 3.0 (2H, CH_2 quartet); 3.43 (2H, $\text{CH}_2\text{-Hg}$ singlet, $J(^1\text{H-}^{199}\text{Hg})$ 255 Hz); 7.33 (4H, C_6H_4 singlet).

Reaction of triene mixture with PhCH_2HgCl . 220 ml (1.5 mmol) of the trienes in ether solution was added over a 2 h period to a solution of 0.49 g (1.5 mmol) of PhCH_2HgCl in 10 ml of THF and 10 ml of Et_2O . The reaction was monitored by paper chromatography. R_f PhCH_2HgCl 0.75, R_f $(\text{PhCH}_2)_2\text{Hg}$ 0.95. After completion of the reaction the solvent was evaporated under reduced pressure and the residue was treated with methanol. Removal of unreacted PhCH_2HgCl (0.35 g) from the filtrate at -40°C gave 0.12 g of a colourless crystalline substance, comprising a mixture of three compounds: $\text{PhCH}_2\text{-HgCl}$, $\text{EtC}_6\text{H}_4\text{CH}_2\text{HgCl}$ and $\text{EtC}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{Ph}$ in 1/1/1 ratio. PMR (δ , ppm): 1.50 (6H, CH_3 multiplet); 2.60 and 2.66 (4H, two $\text{CH}_2\text{-Hg-C}$ singlets, $J(^1\text{H-}^{199}\text{Hg})$ 134 Hz); 2.92 (4H, CH_2 quartet); 3.40 and 3.46 (4H, $\text{CH}_2\text{-Hg-Cl}$ singlets, $J(^1\text{H-}^{199}\text{Hg})$ 252 Hz); 7.26 (18H, C_6H_4 and C_6H_5 multiplet).

Aromatisational stannylation of methylenedihydrobenzenes

Dibenzyl(*o*-ethylbenzyl)chlorostannane. 250 ml of trienes in ether obtained from 0.15 M of PhCH_2MgCl and 0.15 M Et_2SO_4 in 400 ml of ether was added dropwise over an hour to 0.38 g (1 mmol) of $(\text{PhCH}_2)_2\text{SnCl}_2$ in 20 ml of THF while stirring and the mixture was stirred for another hour. The reaction was monitored by paper chromatography, R_f $(\text{PhCH}_2)_2\text{SnCl}_2$ 0.05 (red spot); R_f product 0.97 (yellow spot). After completion of the reaction the solvent was evaporated under vacuum, the residue was extracted 5 times with hot pentane. The extract was evaporated and the crystals so obtained were dissolved in a small amount of benzene and passed through a chromatographic column filled with SiO_2 ($l = 5$ cm, $d = 2.5$ cm). The reaction product was eluted with pentane, the solvent evaporated and the precipitated crystalline colourless substance was purified by recrystallization from pentane, yield 0.19 g (37% with respect to the trienes and 85% in unreacted $(\text{PhCH}_2)_2\text{SnCl}_2$), m.p. 86–87°C. (Found: C, 60.32; H, 5.53; Cl, 7.85. $\text{C}_{23}\text{H}_{25}\text{ClSn}$ calcd.: C, 60.64; H, 5.49; Cl, 7.79%). PMR (CH_2Cl_2 , δ , ppm): 1.13 (3H, CH_3 triplet); 2.34 (2H, CH_2 quartet); 2.63 and 2.69 (6H, two CH_2 singlets); 7.11 (14H, C_6H_4 and C_6H_5 multiplet).

Reductive cleavage of dibenzyl(*o*-ethylbenzyl)chlorostannane *. 0.09 g (0.2 mmol) of previously obtained organotin compound in 5 ml of THF was added dropwise to the boiling suspension of 0.02 g (0.6 mmol) of LiAlH_4 in 5 ml of THF and the reaction mixture was then refluxed for 0.5 h. After completion of the reaction 0.021 g (0.2 mmol) of ethylbenzene was added as a reference. The mixture was quenched with water, extracted with pentane and analysed by quantitative GLC. The reduction products comprised a mixture of toluene and *o*-ethyltoluene (yield 93%).

Ethyl(*o*-ethylbenzyl)dichlorostannane. 280 ml (3 mmol) of an ether solution of trienes, obtained from 0.15 M $(\text{C}_2\text{H}_5)_2\text{SO}_4$ in 400 ml of ether, were added with stirring over an hour to a solution of 1.5 g (6 mmol) of $\text{C}_2\text{H}_5\text{SnCl}_3$ in 30 ml of ether. The reaction was monitored by paper chromatography, R_f $\text{C}_2\text{H}_5\text{SnCl}_3$ 0.1, R_f product 0.9. The solvent and unreacted $\text{C}_2\text{H}_5\text{SnCl}_3$ were evacuated under vacuum and the residue was repeatedly treated with hot hexane. On cooling, colourless crystals precipitated from the extract. Filtration, washing with hexane and drying gave 0.15 g (30% with respect to trienes), m.p. 50–52°C. (Found: C, 39.29; H, 4.92; Sn, 35.10. $\text{C}_{11}\text{H}_{16}\text{Cl}_2\text{Sn}$ calcd.: C, 39.11; H, 4.72; Sn, 35.16%). PMR (CH_2Cl_2 , δ , ppm): 1.16 and 1.58 (8 H, CH_2 and CH_3 multiplet); 2.6 (2H, CH_2 quartet); 3.16 (2H, CH_2 singlet); 7.1 (4H, C_6H_4 multiplet).

Reductive cleavage of the product was carried out according to the technique described above, the reduction product was *o*-ethyltoluene (96%) (GLC data).

Aromatisational germylenation of methylenedihydrobenzenes

Interaction of trienes with GeCl_4 . 50 ml of triene solution was added over a 0.5 h period to the refluxing solution of 0.6 g (2.8 mmol) of GeCl_4 in 15 ml of

* The reduction technique was checked on $(\text{PhCH}_2)_2\text{SnCl}_2$ and $(\text{PhCH}_2)_3\text{SnCl}$ and gave toluene in quantitative yields.

abs. THF while stirring. After refluxing for another hour the reaction mixture was consecutively treated with 2.5 ml of a 1.7 N ether solution of HCl (4.3 mmol) and after further refluxing for 3 hours, with 30 ml of MeMgI (10 mmol) in ether solution. The mixture was refluxed for another 6 h and treated with saturated aqueous NH_4Cl , the ether layer was separated and evaporated. GLC and mass spectrometric analyses did not reveal any organogermanium compounds in the reaction mixture.

Reaction of trienes with dichlorogermylene dioxanate. 100 ml of an ether solution of trienes (6 mmol) was added with stirring over an hour to a refluxing solution of 1.38 g (6 mmol) of $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ in 30 ml of THF. The reaction mixture was heated for another hour and then consecutively treated with 5 ml of a 1.7 N ether solution of HCl and, after refluxing for 3 hours, with 60 ml of MeMgI solution. The reaction mixture was refluxed for another six hours and then the excess of the Grignard reagent was quenched with aqueous NH_4Cl , the reaction products extracted with ether and analyzed by quantitative GLC, yield 18–22%. Running the reaction under argon did not increase the yield.

Interaction of trienes with HGeCl_3 . 70 ml of ether solution of trienes (3.5 mmol) was added over a 0.5 h period to a refluxing solution of 0.72 g (4 mmol) of HGeCl_3 in 20 ml of THF. After refluxing for another hour the reaction mixture was consecutively treated with HCl and MeMgI as described above and then analyzed by GLC and GC/MS. Analyses did not reveal any organogermanium benzyl compounds in the reaction mixture.

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