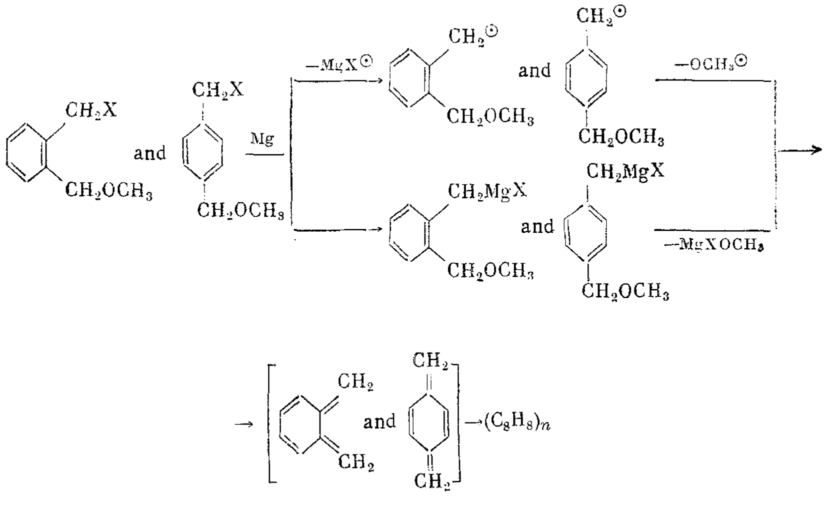
DIRECT AND RETRO PROCESSES OF HETEROORGANIC FRAGMENTATION

4.* PREPARATION AND PROPERTIES OF o- AND p-METHOXYMETHYL-SUBSTITUTED BENZYL DERIVATIVES OF MERCURY AND TIN†

O. A. Reutov, V. A. Nikanorov,
V. I. Rozenberg, and R. I. Gorbacheva

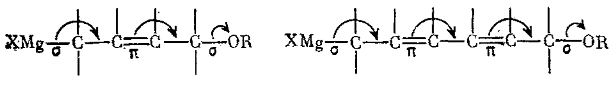
UDC 542.91:547.254.9:547.258.11

Previously we discovered that trienes of the exo-methylenecyclohexadiene type, containing a hydrogen atom as one of the substituents in the geminal node, easily undergo electrophilic aromatization under the influence of metal salts, the so-called "soft" Lewis acids. We previously used this rule when studying the reaction mechanisms in the benzyl organometallic series [1, 3, 4] and in the synthesis of a number of benzyl derivatives of mercury(II) [2], tin(IV) [2, 5], and gold(I) [6]. It also seems of interest to use this rule to synthesize those organometallic compounds (OMC) whose preparation by the usual methods is either difficult or impossible, for example, the o- and p-methoxymethyl-substituted benzyl OMC, which previously could not be obtained in view of the extreme instability of the Grignard reagents [7].



(I)

The question of whether such a reaction direction is caused either by the decomposition of the intermediately formed radical particles or by the manifestation of a strong σ,π conjugation in the ground state of the bond systems depicted below remains unanswered as yet and has independent interest.



However, it is clear that in order to obtain such compounds it is necessary to use a reaction where such polarizable, and consequently exceedingly inclined to undergo fragmentation, conjugation chains do not arise during its course. Such a reaction proved to be aromatization metalation, which opened up new possibilities for obtaining the first members of this class of compounds [8].

---

[*] See [1, 2] for Communications 3 and 5.

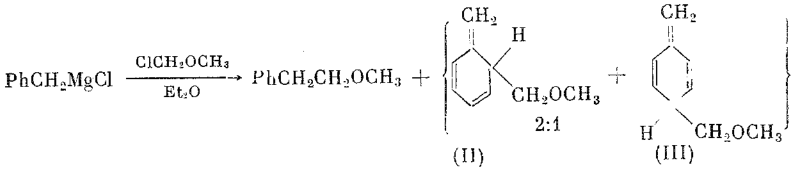
[†] The paper is published by order of the Editorial Board of this journal dated December 6, 1979.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2085-2092, September, 1980. Original article submitted April 18, 1980.

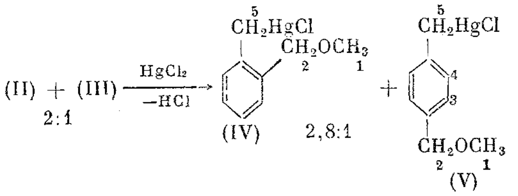
TABLE 1. Dependence of Chemical Shift Values of Protons of o- and p-Methoxymethylbenzylmercury Chlorides on Addition of Eu-(fod)$_3$

Compound	R	Chemical shift δ, ppm				
		H^1	H^2	H^3	H^4	H^5
(IV)	0	3,35	4,55			3,13
	0,1	3,66	4,86			3,22
	0,2	3,94	5,14			3,29
	0,3	4,31	5,52			3,38
tg α		1	1,01			0,26
(V)	0	3,32	4,37			3,23
	0,1	9,13	10,42	9,28	7,72	3,53
	0,2	12,29	13,77	10,44	8,07	3,72
	0,3	15,38	16,95	11,57	8,34	3,92
tg α		1	1,05	0,36	0,10	0,06

As the starting semiquinoid systems for obtaining the indicated OMC we used a mixture of the 6- and 4-methoxymethyl-substituted methylenedihydrobenzenes, which was obtained in 20% yield as described in [9] from benzylmagnesium chloride and chloromethyl methyl ether, followed by treatment of the reaction mixture with saturated aqueous NH_4Cl solution.



Exothermic reaction was observed when an ether solution of trienes (II) and (III) was treated with $HgCl_2$, which reaction proceeded with the evolution of 1 equiv. of HCl and led to the formation of a mixture of two organomercury compounds (OHgC) in 85% yield.



The elemental composition of the (IV)-(V) mixture corresponded to the formula $C_9H_{11}ClHgO$, while the UV spectrum represented a flattened line with a high absorption intensity and a maximum at 249 nm, which is characteristic for benzyl derivatives of mercury. The PMR spectrum of the reaction product has two signals of the protons of the CH_2Hg group and two signals of the protons of the CH_2O group, i.e., the product represents a mixture of two isomers in a 2.8:1 ratio.

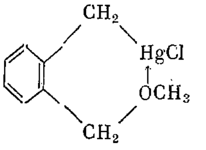
A mixture of (IV) and (V), purified by recrystallization, was studied by the PMR spectroscopy method, employing Eu(fod)$_3$ as the paramagnetic shift reagent (PSR) and the "standard proton" method [10], a procedure that is usually used when studying structurally related compounds. As the signal of the standard proton we used the signal of the methyl protons of the CH_2OCH_3 grouping, which functions as the complexing center with the Eu atom.

With successively increasing amounts of added Eu(fod)$_3$ the signals successively shifted downfield, in which connection the shift was more rapid for the signals of the isomer that was present in lower concentration. Even when R = 0.1 (R is the ratio of the mole concentrations of the PSR to the substrate) the spectrum of an AB system, corresponding to a p-disubstituted benzene, appeared in the absorption region of the aromatic protons. This made it possible to identify the isomer, found in the mixture in lower concentration, as being p-methoxymethylbenzylmercury chloride (V).

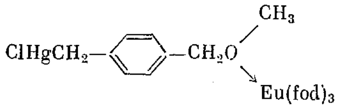
Obtaining a direct spectrum for the predominant isomer is made difficult by the very small shift of its signals even at high concentrations of the PSR ($R > 0.5$). However, a comparative examination of the relative induced chemical shifts (ICS) of the two OHgC isomers, and also the substantially greater relative shift rate of the signal of the CH_2HgCl group made it possible to identify this compound as being o-methoxymethylbenzylmercury chloride (IV).

In Table 1 are given the ICS of the protons of (IV) and (V) with successively increasing amounts of added $Eu(fod)_3$ and the ratio of the ICS to the shift of the protons of the methoxy group ($\tan \alpha$). The attention is attracted to the fact that the two isomers differ greatly in the ability to form complexes with the employed PSR. An analysis of the obtained data shows that the shift rate of the signals of the protons of the CH_2OCH_3 group in (V) is over 12 times higher than in the o-isomer (VI), despite the predominance of the latter in the mixture.

Since it is known that in the most general case the affinity of the substrate toward the PSR can be regarded as being a measure of the basicity of its nonbonding electron pair, the difference observed by us in the behavior of the two studied OHgC definitely testifies to the fact that (IV) has a much lower ability than the p-isomer (V) to undergo intermolecular coordination with the Eu atom of the PSR. This phenomenon can be explained by the existence of intramolecular coordination of the O and Hg atoms in (IV), which lowers the basicity of the O atom substantially and in this way hinders its intermolecular coordination with the PSR.



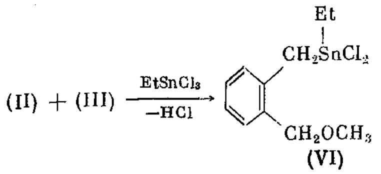
Intramolecular coordination



Intermolecular coordination

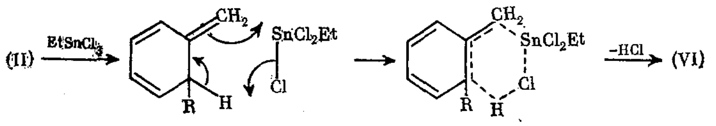
The obtained mixture of (IV) and (V) was separated by chromatography into the pure isomers (mp 60 and 90°C, respectively), whose purity was proved by the PMR method.

Compounds (II) and (III) are also capable of aromatization stannylation [2, 5] ~~when treated with $EtSnCl_3$:~~

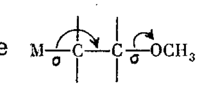


(VI)

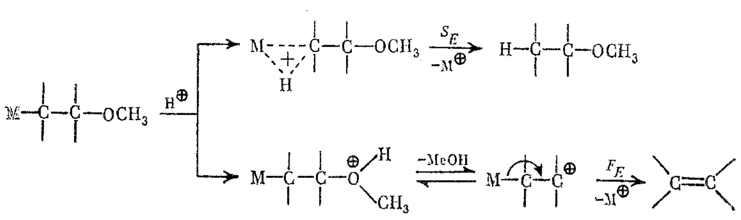
The structure of (VI) was established by the elemental analysis and the PMR and IR spectral data, according to which it contains an o-disubstituted benzene ring (ν 740, 775, and 778 cm^{-1}) and is ethyl(o-methoxymethylbenzyl)dichlorostannane. As a result, this is now the second example observed by us of the peculiar preference shown by the Sn salts of the o-semiquinoid trienes over the p-semiquinoid salts to enter into aromatization stannylation reactions [2]. It may be assumed that the observed phenomenon can be explained by postulating that this reaction proceeds by a coordinated pericyclic mechanism with the formation of a closed aromatic transition state:



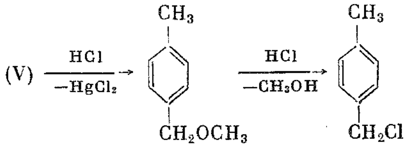
$R = CH_2OCH_3$.

The obtained methoxymethyl-substituted benzyl OMC may be regarded as being phenylogs of β-alkoxyethyl quasi-complexes of type  $M-C-C-OCH_3$, which, as is known [11], can exhibit a dual reactivity in reactions with electrophilic reagents. For example, two transformation paths are possible with protic acids, namely with attack of the C−M bond (electrophilic substitution) and with attack of the O atom (electrophilic fragmentation):

Scheme 1



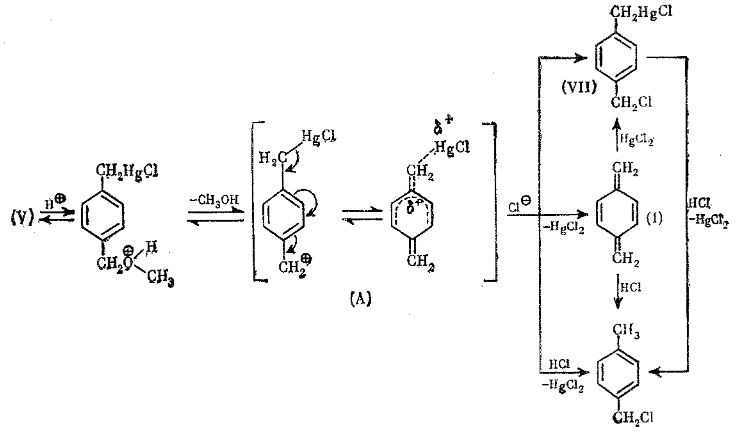
In connection with this analogy, in principle two directions of attack are also possible for the compounds obtained by us. For verification we studied the acid cleavage reaction of (V) by HCl in dioxane. Based on the quantitative GLC data, the main product of this reaction is p-methylbenzyl chloride (98%), whose formation can be explained by the initial protodemercuration of the OHgC and subsequent solvolysis of the intermediate p-methylbenzyl ether:



At first glance, this was supported by the detection of trace amounts of the p-methylbenzyl ether in the acid cleavage products. However, the blank experiments disclosed that under the conditions of the studied reaction the conversion of this ether to the chloride is a total of only 40%, i.e., the above given reactions cannot be the main path for the formation of p-methylbenzyl chloride from (V).

Apparently, another reaction also proceeds in parallel in the studied system, which reaction is related to the initial attack of the O atom in (V) and the formation of a metallomethyl-substituted benzyl cation (A), which is possibly stabilized by the π participation of the ring and the σ participation [1, 12] of the C−Hg bond:

Scheme 2



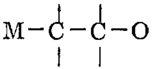
Taking into account the known chemical properties of p-xylylene (I), in particular its ability to enter into 1,6-addition reactions [13, 14], the metalated cationoid intermediate (A) can then undergo attack by Cl^- at the C atom to give either the intermediate (VII) or p-methylbenzyl chloride, or it can underto attack by Cl^- at the Hg atom to give the kinetically independent quinoid compound, which is then stabilized in two ways: by the 1,6-addition of HCl to (I) to give p-methylbenzyl chloride [14], or by the addition of $HgCl_2$ to give (VII) [formally this reaction can be regarded as being the aromatization metalation of (I)].

The proposed reaction scheme is also confirmed by the fact that in some of the experiments the acid cleavage of (V) was accompanied by the formation of small amounts of poly-p-xylylene, while the slight progress of a reaction yielding trace amounts of (VII), which could not be isolated under ordinary conditions in the pure form, was recorded by the TLC method.

However, in harmony with the above proposed reaction scheme, an increase in the yield of (VII) could be expected if the acid cleavage of (V) is run in the presence of added $HgCl_2$, which, on the one hand, should retard the acid cleavage due to a decrease in the nucleophilic coaction and, on the other hand, accelerate exchange of the OMe group by the Cl atom. Also important here is the fact that the addition of excess $HgCl_2$ to the system should increase the contribution of the possible aromatization metalation of (I) when compared with its competing electrophilic aromatization by HCl (a similar effect of adding $HgCl_2$ was observed previously in the acid cleavage reactions of benzylmercury chloride [1]).

Actually, running the reaction for the protodemetalation of (V) in the presence of a fourfold mole excess of $HgCl_2$ increases the yield of (VII) substantially, which was isolated in 10% yield by TLC on silica gel.

The UV spectrum of a solution of (VII) in ethanol represents a flattened line that is characteristic for benzyl OMC, with a maximum at 251 nm and a high extinction coefficient (log ε 4.24). The PMR spectrum of this compound has a singlet in the 3.26 ppm region, which belongs to the protons of the CH_2Hg group, and a singlet of 4.52 ppm, which belongs to the CH_2Cl group. The mass spectrum of (VII) has a quite intense polyisotopic multiplet of a molecular ion with m/e 372-381, which then decomposes into fragment ions with m/e 268-276 ($HgCl_2$), 198-204 (Hg), 139-141 ($ClCH_2C_6H_4CH_2$), and 104 (C_8H_8) respectively. As a result, under electron impact the studied compound is capable of decomposing to give p-xylylene. The structure of (VII) was also confirmed by the results of its acid cleavage by HCl to p-methylbenzyl chloride and $HgCl_2$.

As a result, our study of the properties of a new class of methoxymethyl-substituted benzylmercury chlorides in acid cleavage processes permits the conclusion that a new and unusual reaction direction, related to the replacement of oxygen by halogen with a retention of the C−Hg bond in the molecule, can be realized for these compounds. It is understood that the retention can be only apparent, if it is considered that this reaction can proceed by the fragmentation−addition mechanism (see Scheme 2). However, in any case transformations of this type are encountered very rarely in the chemistry of the OMC [1, 4]. The formation of (VII) also represents interest for the reason that for simpler systems of type  $M-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-O\,R$, whose phenylogs are the compounds synthesized by us, replacing the O atom by Hal atom with retention of the C−M bond has proved impossible up to now, since irreversible heterolytic fragmentation of the molecule with formation of the olefin always occurred when such reactions were attempted (see Scheme 1). It may be assumed that this difference is theoretical and is explained by the fact that heterolytic fragmentation in the series of p-substituted benzyl systems is essentially a reversible process (see Scheme 2) due to the exclusively high polarizability (or softness in terms of the principle of hard and soft acids and base) of quinoid systems when compared with ordinary olefins and their clearly expressed ability to take part in the addition reactions, the reverse of fragmentation, of soft Lewis acids with the formation of aromatic OMC.

EXPERIMENTAL

The PMR spectra were obtained on Varian T-60 and Varian XL-100 instruments using 10-15% solutions in either $CDCl_3$ or CD_3CN. As the standard we used TMS (internal) and HMDS (external). As the shift reagent we used tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-1,6-octanedionato)europium(III) ($Eu(fod)_3$) [10]. The IR spectra in Nujol were taken on a UR-20 instrument. The UV spectra were obtained on a Cary instrument using 0.003 M solutions in either ethanol or dioxane.

The quantitative GLC analysis of the mixture of products from the acid cleavage reactions was run on a Tswett-2 instrument (2.3 m × 4 mm glass column packed with 15% Apiezon L deposited on Chromaton N-AW-DMCS, 0.16-0.20 mesh). At the internal standard we used o-ethyltoluene. For the chromatographic separations we used silica gel L 5/40 μ. For the paper chromatography (PC) we used pentane as the eluent and dithizone as the developer.

The chloromethyl methyl ether and the o- and p-methylbenzyl methyl ethers were obtained by known procedures; the p-methylbenzyl chloride was purified by a triple vacuum-distillation. The ethyltrichlorostannane was obtained as described in [15]. The HCl solution in dioxane was prepared as described in [16]; prior to saturation the abs. dioxane was distilled over $LiAlH_4$.

1-Methylene-6-methoxymethyl-2,4-cyclohexadiene (II) and 1-Methylene-4-methoxymethyl-2,5-cyclohexadiene (III). Trienes (II) and (III) were obtained as described in [9].

o- and p-Methoxymethylbenzylmercury Chlorides (IV) and (V). With stirring, to a solution of 8.13 g (30 mmoles) of $HgCl_2$ in 200 ml of ether was added dropwise, in 30 min, at ~ 20°, 375 ml (30 mmoles) of an ether solution of a mixture of trienes (II) and (III). At the end of reaction (checked by PC) the solvent was distilled in a rotor evaporator, while 70 ml of abs. MeOH was added to the residual oil and the mixture was let stand for 12 h at −50°. The main portion of the mother liquor was decanted from the obtained precipitate and then the crystals were filtered, washed with chilled pentane, and dried in vacuo over paraffin and $CaCl_2$. Recrystallization from hexane gave 9.5 g (85% yield) of a mixture of (IV) and (V), mp 40-45° (mixture of isomers, 2.8:1). Found: C 29.19; H 2.95; Cl 9.79; Hg 53.55%. $C_9H_{11}ClHgO$. Calculated: C 29.11; H 2.96; Cl 9.57; Hg 54.07%.

A solution of 0.8 g of a mixture of (IV) and (V) in the minimum amount of CH_2Cl_2 was transferred to a 21 × 13 cm glass plate, covered with silica gel, and eluted with a 20:1 $CHCl_3$–ethyl acetate mixture. The first fraction with R_f 0.72 (0.56 g) was purified by recrystallization from hexane. Compound (IV) was isolated, mp 60°. The second fraction with R_f 0.6 (0.19 g) was purified by recrystallization from a 5:1 hexane–benzene mixture. We obtained (V), mp 90°.

Ethyl(o-methoxymethylbenzyl)dichlorostannane (VI). To a stirred solution of 3.6 g (14 mmoles) of $EtSnCl_3$ in 20 ml of abs. ether was added dropwise, in 20 min, 190 ml (14 mmoles) of an ether solution of a (II)-(III) mixture. Exothermic reaction was observed here. The mixture was stirred for another hour, after which the solvent was distilled at 40-45° (2 mm). The residue was dissolved in the minimum amount of benzene and chromatographed through a 7 × 2 cm column, packed with silica gel, and eluted with benzene. The front fraction was collected and the eluate was evaporated to give 2.36 g of an oily product, which crystallized spontaneously in 15 min. Compound (VI) was purified by recrystallization from hexane. Yield 2.35 g (50%), mp 84°. Found: C 37.39; H 4.67; Cl 19.73; Sn 32.99%. $C_{11}H_{16}Cl_2OSn$. Calculated: C 37.35; H 4.52; Cl 20.04; Sn 33.55%. PMR spectrum (δ, ppm): 1.18 m and 1.44 m A_2B_3 systems (5H), 3.24 s (2H, CH_2), 3.46 s (3H, CH_3), 4.6 s (2H, CH_2), 7.2 m (4H, C_6H_4). $J_{^1H^{117}Sn} = 95$, $J_{^1H^{119}Sn} = 100$ Hz.

Reaction of p-Methoxymethylbenzylmercury Chloride (V) with HCl in Dioxane. To a solution of 1.11 g (3 mmoles) of (V) in 10 ml of abs. dioxane was added 15 ml of a 2.5 M solution of HCl in dioxane. The reaction mixture, divided into two equal portions, was kept in sealed ampuls for 6 h at 100°. Then the ampuls were opened; the dioxane was vacuum-distilled from the first ampul and the residual crystals were filtered to give 0.4 g (98% yield) of $HgCl_2$.

To the contents of the second ampul were added 0.09 g (0.75 mmole) of o-ethyltoluene as the chromatographic standard and 15 ml of water, after which the acid was neutralized with $NaHCO_3$ and the mixture was extracted with pentane (2 × 10 ml). The pentane extract was dried over $MgSO_4$ and then subjected to quantitative GLC analysis: Here was recorded the formation of p-methylbenzyl chloride (98%) and traces of p-methylbenzyl methyl ether.

p-Chloromethylbenzylmercury Chloride (VII). To a solution of 0.2 g (0.52 mmole) of (V) in 25 ml of dioxane, containing 8 mmoles of HCl, was added 1.54 g (2 mmoles) of $HgCl_2$ and the mixture was kept for 4 h in a sealed ampul at 70°. At the end of reaction the ampul was opened, the dioxane was vacuum-distilled and the solid residue was extracted with $CHCl_3$, which was distilled off, while the residue was dissolved in a little CH_2Cl_2 and chromatographed in a thick layer of silica gel, using a 20:1 $CHCl_3$–ethyl acetate mixture for elution. The fraction with R_f 0.78 was collected, extracted with CH_2Cl_2, the solvent was distilled off, and the solid residue was washed with chilled pentane and dried in vacuo. The yield of (VII) was 0.02 g (10%), mp 94-95° (in a sealed capillary, with decompn.). PMR spectrum ($CDCl_3$, δ, ppm): 3.26 s (2H, CH_2), 4.52 s (2H, CH_2), 7.20 m (C_6H_4).

The authors express their gratitude to N. D. Sergeeva for assistance in taking and discussing the PMR spectra, and to O. S. Chizov for obtaining the mass spectrum of p-chloromethylbenzylmercury chloride.

CONCLUSIONS

1. The aromatization metalation of 1-methylene-6-methoxymethyl-2,4-cyclohexadiene and 1-methylene-4-methoxymethyl-2,5-cyclohexadiene by treatment with $HgCl_2$ in ether gave the first members of a previously unavailable class of organometallic compounds, and specifically the o- and p-methoxymethylbenzylmercury chlorides.

2. The reaction of a mixture of the indicated trienes with $EtSnCl_3$ leads to the exclusive formation of the o-methoxymethyl-substituted benzyl organotin compound, which is apparently explained by the coordinated pericyclic mechanism of the aromatization stannylation reaction.

3. A study of the obtained organomercury compounds by the PMR method using a paramagnetic shift reagent disclosed the presence of an intramolecular coordination of the O atom at the Hg atom in o-methoxymethylbenzylmercury chloride.

4. p-Methoxymethylbenzylmercury chloride exhibits a dual reactivity in the acid cleavage reaction using HCl, which is due to electrophilic attack of the O atom and C−Hg bond.

5. When p-methoxymethylbenzylmercury chloride is reacted with HCl in the presence of added $HgCl_2$ a previously unknown type of acid cleavage of β-alkoxyethyl organomercury compounds was observed, and specifically replacement of the O atom by halogen atom with the formal retention of the C−Hg bond and the formation of p-chloromethylbenzylmercury chloride.

LITERATURE CITED

1. V. A. Nikanorov, V. I. Rozenberg, M. Abazeed, Yu. G. Bundel, and O. A. Reutov, J. Organomet. Chem., 108, 325 (1976).
2. O. A. Reutov, V. I. Rozenberg, R. I. Gorbacheva, and V. A. Nikanorov, J. Organomet. Chem., 201 (1980).
3. V. I. Rozenberg, V. A. Nikanorov, V. I. Salikova, Yu. G. Bundel', and O. A. Reutov, Dokl. Akad. Nauk SSSR, 223, 879 (1975).
4. V. I. Rozenberg, V. A. Nikanorov, R. I. Gorbacheva, Yu. G. Bundel', and O. A. Reutov, Dokl. Akad. Nauk SSSR, 224, 833 (1975).
5. Inventor's Certificate No. 595,326, Nov. 12, 1976; Byull. Izobr., No. 8 (1978).
6. V. I. Rozenberg, R. I. Gorbacheva, E. I. Smyslova, K. I. Grandberg, V. A. Nikanorov, Yu. G. Bundel', and O. A. Reutov, Dokl. Akad. Nauk SSSR, 225, 1082 (1975).
7. F. G. Mann and F. H. C. Stewart, J. Chem. Soc., 2826 (1954).
8. V. A. Nikanorov, V. I. Rozenberg, R. I. Gorbacheva, Yu. G. Bundel', and O. A. Reutov, Zh. Org. Khim., 11, 2441 (1975).
9. R. A. Benkeser and W. De Talvo, J. Am. Chem. Soc., 89, 2141 (1967).
10. D. R. Kelsey, J. Am. Chem. Soc., 94, 1764 (1972).
11. A. N. Nesmeyanov, Uch. Zap. Mosk. Univ., No. 132 (1950), Org. Khim., Vol. 7, p. 5.
12. W. Hanstein, H. J. Berwin, and T. G. Traylor, J. Am. Chem. Soc., 92, 829 (1970).
13. A. T. Kalashnik, Dissertation, Moscow (1967).
14. L. A. Errede, J. M. Hoyt, and R. S. Gregorian, J. Am. Chem. Soc., 82, 5224 (1960).
15. W. P. Neumann and G. Burkhardt, Ann. Chem., 663, 11 (1963).
16. H. C. Brown and C. Groot, J. Am. Chem. Soc., 64, 2223 (1942).

SYNTHESIS OF ESTER AND AMIDE DERIVATIVES OF PLATINUM AND PALLADIUM METALCARBOXYLIC ACIDS BY THE ORGANOMERCURY METHOD

V. I. Sokolov, G. Z. Suleimanov,
A. A. Musaev, and O. A. Reutov

UDC 542.91:547.1'13:546.98:546.92

The derivatives of metalcarboxylic acids attract attention in connection with a study of the reaction of CO and CO_2 with the complexes of transition metals [1]. The esters, amides, and in some cases also the salts of metalcarboxylic acids can be obtained as stable compounds, whereas the acids themselves, except for individual examples, are usually unstable [2]. The carboxamide derivatives of Pt and Pd are unknown. The alkoxycarbonyl monoderivatives are synthesized either by the carbonylation of L_2MCl_2 in methanol [3-7] or by the oxidative addition of chlorocarbonic esters to $L_nM(0)$ [4]. A brief communication [8] on the insertion $(Ph_3P)_3$-Pt(0) at the C−C bond of dimethyl oxalate lacks adequate proof.

The general synthesis of the Pt and Pd σ derivatives by the reaction of their zero-valence complexes with organomercury compounds [9, 10] is convenient for obtaining the carboxyl derivatives, since the corresponding ester [11, 12] and amide [13] derivatives of the mercuricarboxylic acids are known. The reaction of

---

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2093-2096, September, 1980. Original article submitted October 20, 1979.