Journal of Organometallic Chemistry, 88 (1975) 315—320

ARYLMERCURY COMPOUNDS

IV*. SYMMETRIZATION IN THE ABSENCE OF AUXILIARY LIGAND

YUVAL HALPERN* and NISSIM GARTI
The Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem (Israel)

(Received September 9th, 1974)

Summary

Phenylmercuric acetate is converted into diphenylmercury via a symmetrization process, in the absence of an auxiliary ligand, when the reaction is carried out at $6.5 \geqslant pH > 4.0$. Arylmercuric salts, in which the aromatic rings contain more than one electron donating group, symmetrize in the absence of an auxiliary ligand when the reaction is carried out at a basic pH. Both processes can be carried out in water or in mixtures of organic solvents and water.

The factors influencing the symmetrization at different pH values are discussed.

Introduction

The general symmetrization process [1] is summarized in eqn. 1**. In order to throw further light on this process and to study the reaction mechanism, the reaction was carried out under a variety of conditions as published hitherto [1,2]. No symmetrization takes place in the absence of a chelating agent. On the other hand, conditions exist under which the reaction proceeds with different chelating agents but in the absence of an auxiliary ligand. The latter discovery simplifies the process and leads to further saving in materials, which may be of particular interest for industry, in addition to the recyclization process [2].

$$2ArHgX + Che\cdot Na_x \xrightarrow{\text{Auxiliary ligand}} Ar_2Hg + Hg\cdot Che(complex) \qquad (1)$$

---

[*] For part III see ref. 13.

[**] Che = chelating agent.

Results

A. Symmetrization under acidic pH

Phenylmercuric acetate symmetrizes in distilled water in the presence of EDTA·Na_4 (ethylene diaminetetraacetic acid tetrasodium salt) in the absence of an auxiliary ligand. The reaction yield is only 17-19% (compared with 95% when the reaction is carried out in the presence of ammonia [1]). The relatively low yield is a result of the fact that on adding the chelating agent to an acidic solution (pH 4.3) of the mercuric salt, a white precipitate of C_6H_5Hg·Che(salt) is formed, which does not participate in the process. Only a small fraction of the chelating agent forms an active complex with the arylmercuric salt, which then symmetrizes.

No symmetrization takes place when using chelating agents in the free acid form (H_4EDTA, H_4CDTA) or when increasing the pH of the system to pH values > 7 (using NaOH as a base). On the other hand the process takes place with 12-17% yields using H·EDTA·Na_3 or H_2·EDTA·Na_2.

NTA·Na_3 (nitrilotriacetic acid trisodium salt) does not promote symmetrization since its addition to the aqueous solution of phenylmercuric acetate renders the solution basic. Use of the free acid (H_3·NTA) causes quantitative precipitation of C_6H_5·NTA (salt), and hence no symmetrization takes place. DAETA·Na_4 ([ethylenebis(oxyethylenenitrilo)]tetraacetic acid) which fails to promote a

TABLE 1

DIARYLMERCURIES PREPARED BY THE SYMMETRIZATION PROCESS IN THE PRESENCE OF EDTA·Na_4 BUT IN THE ABSENCE OF A NUCLEOPHILE

$$2ArHgOAc + EDTA\cdot Na_4 \xrightarrow[24\ h]{OH^-} Ar_2Hg$$

Aryl	Solvent	M.p. (°C) (Lit.)	Yield (%)	Analysis found (calcd.)* (%)	
				C	H
Xylyl (2,4)	H_2O/EtOH	172(172) [7]	60	46.46 (46.76)	4.30 (4.38)
Xylyl (2,4)	H_2O	172(172) [7]	66	46.36 (46.76)	4.29 (4.38)
Mesityl (2,4,6)	H_2O/EtOH	242(236) [8]	92	49.05 (49.31)	4.98 (5.02)
Pseudocumyl (2,4,5)[a]	H_2O/Dioxane	189(189) [8]	44	48.99 (49.31)	4.89 (5.02)
Duryl (2,3,5,6)	H_2O/EtOH	242(243 [9]	87	50.92 (51.41)	5.57 (5.57)
Isoduryl (2,3,4,6)	H_2O/Dioxane	218(218) [9]	42	50.91 (51.41)	5.50 (5.57)
Pentamethylbenzene[a]	H_2O	290(278) [9]	81	52.58 (53.33)	5.90 (6.06)
α-Naphthyl	H_2O/EtOH	244(243) [10]	75	52.36 (52.79)	3.00 (3.08)
α-Thienyl[b]	H_2O/Et_2CO	202(199) [1]	94	26.40 (26.19)	1.67 (1.64)
α-Furyl[b]	H_2O	114(114) [12]	70	28.05 (28.69)	1.70 (1.79)

[a] Starting material contains small amounts of impurities which could not be removed by repeated recrystallization. [b] Starting materials were the corresponding chlorides.

reaction in the presence of an auxiliary ligand [1], also fails to promote a reaction in the absence of an auxiliary ligand since it causes the reaction mixture to become basic. The free acid ($H_4 \cdot$DAETA), on the other hand, is found to be useful in the process and results in a 22% yield of diphenylmercury.

B. Symmetrization under basic pH

Symmetrization under basic conditions in the absence of an auxiliary ligand results in high yields with arylmercuric salts in which the aromatic ring contains more than one electron-donating group, e.g. *meta*-xylylmercuric acetate, mesitylmercuric acetate, durylmercuric acetate*, and with other electron-rich aromatic or heterocyclic rings, e.g. α-naphthylmercuric acetate, α-thienylmercuric chloride and α-furylmercuric chloride. Yields of the symmetrization products are summarized in Table 1. Since most of the starting materials leading to the products listed in Table 1 are insoluble in water, the symmetrization process is carried out in a mixture of organic solvent and water [13].

In order to simplify the discussion, the formation of di-*meta*-xylyl- and dimesityl-mercury are chosen to exemplify the process. Figures 1 and 2 depict the reaction rates and yields of di-*meta*-xylyl- and dimesityl-mercury obtained under various reaction conditions.

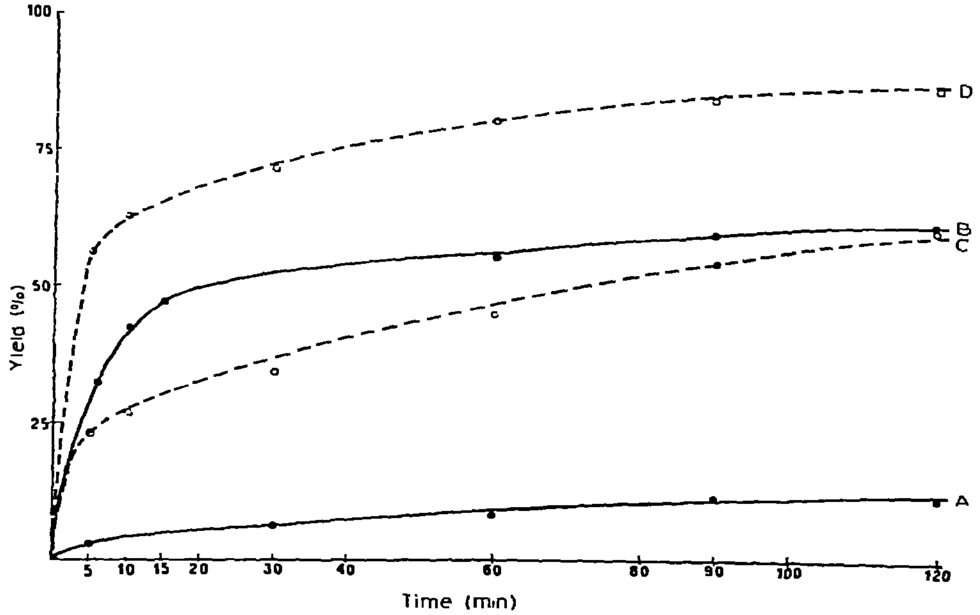

Fig. 1. Symmetrization of *meta*-xylylmercuric acetate and mesitylmercuric acetate, in H_2O/EtOH solution in the presence of EDTA·Na_4. A = Di-*meta*-xylylmercury obtained in the absence of a nucleophile. B = Di-*meta*-xylylmercury obtained in the presence of five-fold excess n-butylamine. C = Dimesitylmercury obtained in the absence of a nucleophile. D = Dimesitylmercury obtained in the presence of five-fold excess n-butylamine.

---

* Mesityl = 2,4,6-trimethylphenyl; duryl = 2,3,5,6-tetramethylphenyl.

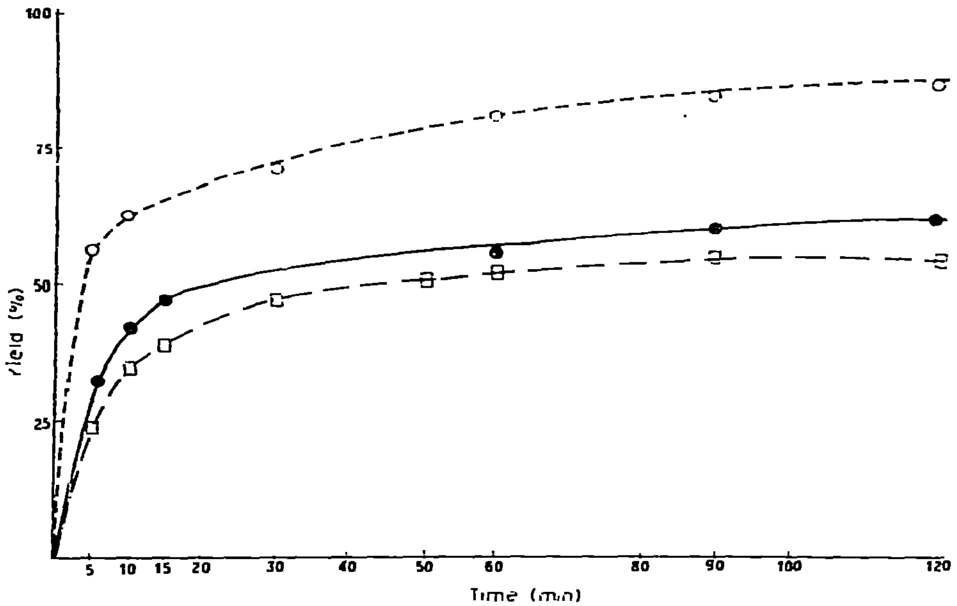

Fig. 2. Formation of diphenylmercury, di-*meta*-xylylmercury and dimesitylmercury via the symmetrization process in H_2O/EtOH solution and in the presence of EDTA Na_4 and n-butylamine. □ = Diphenylmercury. ● = Di-*meta*-xylylmercury. ○ = Dimesitylmercury.

Discussion

An essential step in the symmetrization process is complex formation between the chelating agent and the arylmercuric salt*. Under acidic conditions ($pH < 4.3$) the chelating agent exists as a monosodium salt [3] and hence an insoluble arylmercuric chelating agent salt rather than a complex is formed [4]. At high pH values ($12 > pH > 8$) a stable, soluble complex is obtained, and no symmetrization takes place unless an auxiliary ligand is added. Under mildly acidic conditions ($6.5 > pH > 4.3$) an unstable chelate is formed (in addition to an insoluble salt and a stable complex) in which only part of the carboxylic and amine groups of the chelating agent participate in complex formation. This unstable complex which is attacked by an electrophile ($ArHg^+$) yields the symmetrization product (eqn. 2).

$$ArHg^+ + ArHg(Che)^{-n+1} \rightarrow Ar_2Hg + Hg(Che)^{-n+2} \qquad (2)$$

Regarding the symmetrization at different pH values, the efficiency of the chelating agents is dictated by their dissociation constants [4] and the nature of the chelating agent.

The combination of these factors accounts for the difference in behavior of NTA (which forms an insoluble salt with ArHgX) and DAETA (which forms an unstable, active complex) under the same reaction conditions.

In contrast to inhibition of the reaction at low pH values due to salt formation, the reaction at high pH values is hindered as a result of stable complex for-

---

* A detailed discussion of the symmetrization mechanism will be published in part VI of this series.

mation (between ArHgX and the chelating agent). Under these circumstances the reaction proceeds only by increasing the nucleophilicity of the C—Hg bond and thus enhancing its susceptibility to cleavage by the weak $ArHg^+$ electrophile. The increased nucleophilicity is achieved in either of the following ways: (*a*) By using an auxiliary ligand (ammonia or amine) which by exchanging one or more carboxylic groups [5] in the complex and by donating *n* electrons to the mercury *d* orbitals causes an increase in electron density in the C—Hg bond. This mechanism was established through the results published in Part I of this series [13]. (*b*) By attaching electron-donating groups on the aromatic ring of the arylmercuric salt which also results in electron enrichment of the C—Hg bond (due to inductive and mesomeric effects) to such a degree that the reaction proceeds without the assistance of an auxiliary ligand. Figure 1 shows the correlation between the electron-donating ability of the substituent and the reaction rate and shows that the symmetrization rate increases with the electron-donating ability of the aromatic ring. Furthermore, addition of an auxiliary ligand to such a system will result in reaction rate enhancement (as shown in Fig. 2) for the symmetrization of *meta*-xylyl- and mesityl-mercuric acetate compared with that of phenylmercuric acetate.

Table 1 reveals that steric factors also play an important role in determining the yields obtained in the symmetrization process. For example, isodurylmercuric acetate which has a greater electron-donating ability than mesitylmercuric acetate yields only 42% of the symmetrization product whereas mesitylmercuric acetate yields 92% of dimesitylmercury. This difference in reaction yield is attributed to greater steric hindrance in the duryl- than in the mesitylmercuric acetate. This last observation and its explanation are in agreement with the results obtained for mercuration of mesitylene and durene [6].

Experimental

Arylmercuric salts were prepared by direct mercuration of the corresponding aromatic compounds. Chelating agents and amines were C.P. grade, commercially available materials.

Symmetrization under acidic pH

(*a*). Phenylmercuric acetate (0.672 g, 2×10^{-3} mol) was dissolved in 200 ml distilled water (pH of the resulting solution was 4.3), and a solution of $EDTA \cdot Na_4$ (0.380 g, 10^{-3} mol) in 10 ml distilled water was added with stirring (the pH of the reaction mixture increased to 6.5). After 24 h of stirring, 10 ml 1 *M* NaOH solution were added to dissolve the $C_6H_5Hg \cdot EDTA$ salt. The remaining white solid was filtered, vacuum dried and identified as diphenylmercury. Yield 17%, m.p. 128°. (Found: C, 40.55; H, 2,79. $C_{12}H_{10}Hg$ calcd.: C, 40.62; H, 2,82%.)

(*b*). Phenylmercuric acetate (0.672 g, 2×10^{-3} mol) was dissolved in 200 ml distilled water (pH 4.3). NTA (0.191 g, 10^{-3} mol) in 10 ml distilled water was added while stirring (pH 6.0). The white precipitate collected after 24 h was identified as $C_6H_5OOCCH_2 \cdot N(CH_2COOH)_2$. (Found: C, 31.23; H, 2.99; N, 2.60. $C_{12}H_{13}NO_6$ calcd.: C, 31.93; H, 3.04; N, 2.66%.)

Symmetrization under basic pH

The procedure is exemplified through the symmetrization of mesitylmercuric acetate. Mesitylmercuric acetate (0.756 g, 2×10^{-3} mol) was dissolved in a mixture of 75 ml ethanol and 125 ml distilled water. Dilute NaOH solution was added until a pH of 7 was obtained. $EDTA \cdot Na_4$ (0.380 g, 10^{-3} mol) in 10 ml distilled water was added while stirring. The white dimesitylmercury was collected and vacuum dried after a pre-determined reaction time. The yield after 24 h was 92%, m.p. 242°. (Found: C, 49.05; H, 4.98. $C_{18}H_{22}Hg$ calcd.: C, 49.31; H, 5.02%.)

Acknowledgement

The authors wish to thank Professor M. Levy of The Weizmann Institute of Science, for his helpful comments and discussion.

References

1 N. Garti and Y. Halpern, J. Appl. Chem. Biotechnol., in press.
2 Y. Halpern and N. Garti, Ind. Eng. Chem. Prod. Res. Develop., in press.
3 R.L. Pecsok, J. Chem. Educ., 29 (1952) 597.
4 A.E. Martell, J. Chem. Educ., 29 (1952) 270.
5 F.P. Dwyer and D.P. Mellor, Chelating Agents and Metal Chelates, Academic Press, New York and London, 1964, p. 294.
6 H.C. Brown and C.W. McGary, Jr., J. Amer. Chem. Soc., 77 (1955) 2300, 2306, 2310.
7 J. Weller, Ber., 20 (1887) 1719.
8 A. Michaelis, Ber., 28 (1895) 591.
9 L.I. Smith and F.L. Taylor, J. Amer. Chem. Soc., 57 (1935) 2370.
10 R. Otto, Liebigs Ann. Chem., 147 (1868) 167.
11 W. von Steinkopt and M. Bauermeister, Liebigs Ann. Chem., 403 (1914) 61.
12 H. Gilman and F.G. Wright, J. Amer. Chem. Soc., 55 (1933) 3302.
13 N. Garti and Y. Halpern, J. Appl. Chem. Biotechnol., in press.