Journal of Organometallic Chemistry, 235 (1982) 127—133
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

INTERACTION OF XENON DIFLUORIDE WITH ORGANOMERCURY COMPOUNDS

K.P. BUTIN *, YU.M. KISELEV, T.V. MAGDESIEVA and O.A. REUTOV

Chemistry Department, Moscow State University, Moscow B-234 (U.S.S.R.)

(Received March 30th, 1982)

Summary

XeF_2 is shown to react with organomercury compounds, R_2Hg ($R = PhC{\equiv}C$, p-$MeOC_6H_4$, p-$Me_2NC_6H_4$, p-$EtO_2CC_6H_4$ and $PhCH_2$), with cleavage of the C—Hg bond. The products of the reaction are the following: Xe, RHgF (or $RHgF/HgF_2$ mixture; for R = benzyl RHgF undergoes fast demercurization), RF (excluding $R = PhC{\equiv}C$), R_2, and the products of radical, $R\cdot$, reactions with solvents (dry CCl_4 or $CHCl_3$).

The ease of reaction, about which one can judge from the temperature of the beginning of Xe evolution (given in brackets in °C), was found to decrease in the following sequence: $R = PhCH_2$ (—45) p-$Me_2NC_6H_4$ (—40), $PhC{\equiv}C$ (—5), p-$MeOC_6H_4$ (5), p-$EtO_2CC_6H_4$ (25). This sequence indicates XeF_2 to be an electron acceptor and R_2Hg an electron donor. It follows from the reaction mixture composition that the reaction goes via free radicals. The absence of fluorinated organomercury products in the reaction mixtures may be considered as evidence that XeF_2 reacts more easily with the C—Hg bond than with C—H or C—C bonds.

XeF_2 reacts also with HgX_2 (X = Cl, Br, I) under mild conditions to give X_2, HgF_2, and Xe in quantitative yields.

In papers published during the last decade XeF_2 was shown to be a convenient fluorinating agent for different types of organic compounds. It readily adds fluorine to multiple bonds, causes facile substitution on aromatic centres, and can serve as an oxidizing agent. However, the interaction of XeF_2 with organometallic compounds was practically not studied. The only paper [1] which was published in this field reports that Si—Cl bonds in organosilicon chlorides can be ruptured easily whereas Si—H and Si—C bonds are non-reactive.

The behaviour of organomercury compounds in the presence of XeF_2 have not yet been studied. It is only known that the hard fluorinating agent, elemental F_2, substitutes hydrogen in alkyl groups of organomercury compounds for fluorine, while rupture of the C—Hg bond is a by-process [2].

In this paper we wish to report the results of GC-MS studies of reaction of XeF_2 with a number of organomercury compounds and inorganic mercury(II) halides.

Reaction with Hg^{II} halides

We found that XeF_2 reacts with mercury(II) halides, giving HgF_2, molecular halogens and xenon both in solid phase as well as in CCl_4 solutions (eq. 1). The HgF_2 was identified using X-ray powder analysis (primitive cubic lattice; a_0 = 553 pm).

$$HgHal_2 + XeF_2 \rightarrow HgF_2 + Hal_2 + Xe \qquad (1)$$

Hal = Cl, Br, I

In accordance with Hg—halogen bond energies (Hg—I 254.1; Hg—Br 299.7; Hg—Cl 353.6; Hg—F 384.7 kJ/mole [3]) the fluorination occurs most easily in the case of HgI_2. The solid phase mixing of HgI_2 and XeF_2 at 20°C results in an explosion with instantaneous evolution of iodine vapor.

Interaction with organomercury compounds

Interactions of XeF_2 with symmetrical organomercury compounds, R_2Hg ($R = PhC{\equiv}C$, $PhCH_2$, p-$CH_3OC_6H_4$, p-$(CH_3)_2NC_6H_4$, and p-$EtO_2CC_6H_4$), were carried out in CCl_4 or $CHCl_3$ solutions in argon atmosphere. The results are given in Table 1. The solutions of R_2Hg in these solvents were cooled in an acetone/dry ice bath and then the temperature of the reaction mixture was increased gradually until the xenon gas evolution began. With $(PhCH_2)_2Hg$, Xe began to evolve at ca. —45°C, while with $(EtO_2CC_6H_4)_2Hg$ only at 25°C. The temperature of the start of reaction may be considered as a measure of the relative reactivities of the organomercury compounds, which may thus be arranged in the following sequence of reactivity decreases:

$$R = PhCH_2\ (-45^\circ C) > p\text{-}Me_2NC_6H_4\ (-40^\circ C) > PhC{\equiv}C\ (-5^\circ C) > p\text{-}MeOC_6H_4\ (5^\circ C) > p\text{-}EtO_2CC_6H_4\ (25^\circ C)$$

Thus, the C(benzylic)—mercury bond is the most reactive, and *para*-substituent effects on the reactivity of the diarylmercurials are similar to those in electrophilic aromatic substitution. The general scheme of the reaction, as follows from the results of GC-MS analysis of the reaction mixture, may be written as:

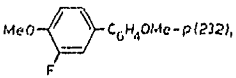
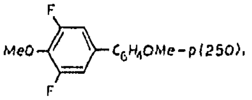
$$R_2Hg + XeF_2 \xrightarrow[\text{or } CHCl_3]{\text{in } CCl_4} RHgF(HgF_2) + RF + Xe + R_2 +$$

+ products of reactions of $R^\cdot$ and $F^\cdot$ radicals with the solvents

In the case of two organomercury compounds, $R = PhC{\equiv}C$ and p-$Me_2NC_6H_4$, the corresponding organomercury fluorides, RHgF can be isolated with the yields of 45—85%. When $R = p$-$MeOC_6H_4$ or p-$EtO_2CC_6H_4$ a partial cleavage of the second C—Hg bond occurs and results in HgF_2 formation, possibly a result

TABLE 1

INTERACTION OF R_2Hg WITH XeF_2

R in R_2Hg	Solvent	Temperature of the reaction (°C) [a]	Yield (%)		Other reaction products (*m/e* values)
			Xe	RHgF	
PhC≡C [b]	$CHCl_3$ (Et_4NBr) [c]	−5	93	46	PhC≡CBr(181) [d,e], $PhCOCH_3$(120), $(PhC{\equiv}C)_2$ (202), PhC≡CH(102),
p-$Me_2NC_6H_4$	$CHCl_3$	−40	91	85	p-$Me_2NC_6H_4F$(139), p-$Me_2NC_6H_5$(121) [e], $(p\text{-}MeOC_6H_4)_2$(240) $PhN(CH_3)CH_2Cl$(155), p-$Me_2NC_6H_4CH_3$(135), p-$Me_2NC_6H_4C_2H_5$(149),
p-$MeOC_6H_4$	CCl_4	5	81	f	p-$MeOC_6H_4F$(126) [c], p-$MeOC_6H_4Cl$(142), $(p\text{-}MeOC_6H_4)_2$(214),  
$PhCH_2$	CCl_4	−45	80	—	$PhCH_2F$(126) [e], $(PhCH_2)_2$(182), p-$CH_3C_6H_4CH_2Ph$(182)
p-$EtO_2CC_6H_4$	CCl_4	25	88	f	p-$EtO_2CC_6H_4F$(158) [g]

[a] Temperatures at the start of Xe evolution. [b] With a six-fold XeF_2 excess the yield of RHgF was 86%. [c] Et_4NBr was added after finishing of Xe evolution at −5°C. [d] Isolated with 43% yield. [e] The major product. [f] $RHgF/HgF_2$ mixture; see the text. [g] Isolated with 71% yield.

of the relatively high reaction temperature (5 or 25°C).

Organofluorides, RF, are formed in all cases, but with different yields depending on the nature of R. The yields are the highest for R = p-$EtO_2CC_6H_4$ and p-$MeOC_6H_4$ which confirms the cleavage of both C—Hg bonds in these organomercurials. Since PhC≡CF is unstable at room temperature and easily polymerizes [4] it cannot be isolated from the reaction mixture. In order to prove the possibility of PhC≡CF formation the reaction was carried out at −5°C, and after completion of Xe gas evolution, Et_4NBr was added to the reaction mixture. PhC≡CBr was isolated with 43% yield, probably from reaction 3.

$$\mathrm{PhC{\equiv}CF\ (in\ situ) + Br^- \rightarrow PhC{\equiv}CBr + F^-} \tag{3}$$

With dibenzylmercury a complex product mixture was obtained, the yield of $PhCH_2F$ being low (Table 1).

In no case did XeF_2 react with the substituents on the aromatic nucleus of diarylmercury compounds with C—Hg bond retention. It is known that aromatic compounds with electron-withdrawing substituents do not react with XeF_2, unless a catalyst, anhydrous HF, is added [e.g. 5]. With organomercurials the reaction proceeds without any catalyst, however. This means that C—Hg bond cleavage proceeds more easily than C—H bond cleavage in an aromatic nucleus under the influence of XeF_2.

In all cases interactions with the solvents were observed. When the reactions were carried out without any solvent, in the solid phase, they were very rapid (explosive in the case of $(PhC{\equiv}C)_2Hg$), and a black "carbonic" substance as well as mercury metal were formed.

The amounts of Xe gas evolved were measured in each experiment. The data obtained (Table 1) show that xenon-containing products do not remain in the reaction mixtures, but the formation of organoxenon intermediates cannot be excluded. From the composition of the reaction products we propose the following simple reaction scheme without involvement of organoxenon compounds (scheme 1).

SCHEME 1.

$$\underset{(D)}{\mathrm{R_2Hg}} + \underset{(A)}{\mathrm{XeF_2}} \rightarrow \underset{(DA)}{[\mathrm{R_2Hg \cdot XeF_2}]} \xrightarrow[\text{transfer}]{\text{charge}} \underset{(D^+A^-)}{[\mathrm{R_2Hg^{\cdot +}\ XeF_2^{\cdot -}}]}$$

$$\downarrow$$

$$\mathrm{RHg^+ + F^- + R\cdot + XeF\cdot}$$

$$\mathrm{RHg^+ + F^-} \rightarrow \mathrm{RHgF} \qquad \mathrm{XeF\cdot} \rightarrow \mathrm{F\cdot + Xe}$$

$$\mathrm{2R\cdot \rightarrow R_2}$$

$$\mathrm{R\cdot + F\cdot \rightarrow RF}$$

$$\mathrm{R\cdot + CCl_4 \rightarrow RCl + \cdot CCl_3}$$

$$\mathrm{R\cdot + CHCl_3 \rightarrow RH + \cdot CCl_3}$$

etc.

D = donor
A = acceptor

The XeF_2/HgR_2 reaction occurs via a donor-acceptor type interaction followed by a one-electron oxidation of R_2Hg yielding in an organomercury cation-radical and the $XeF_2^{\cdot -}$ anion-radical. Then the cation-radical decomposes to the respective cation, RHg^+, and radical, $R\cdot$, while $XeF_2^{-\cdot}$ decomposes to Xe, F^- anion, and $F\cdot$ radical.

C—Hg bond cleavage in organomercury fluorides under the action of XeF_2, which occurs at higher temperatures, may be represented by Scheme 2.

SCHEME 2

$$\begin{tikzcd} RHgF + XeF_2 \arrow[r] & RHgF^{+\cdot} + F^- + XeF\cdot \arrow[r] \arrow[d] & \text{etc.} \\ \text{etc.} & R\cdot + HgF^+ \arrow[l] \arrow[r, "F^-"] & HgF_2 \end{tikzcd}$$

The fate of the radical, $R\cdot$, is analogous to that represented in Scheme 2.

Experimental

PMR spectra were obtained with a Varian T-60 spectrometer; TMS was used as internal standard. Mass spectra were obtained with a Varian MAT-111 GC-MS instrument; column 1,5 m, ϕ 1.8 mm; adsorbent Chromaton-N; phase OV-1 3%, gas He 12.5 ml/min.

Materials

Bis(phenylethynyl)mercury was prepared by interaction of phenylacetylene with K_2HgI_4 as previously described [6]. Bis(*p*-*N*,*N*-dimethylaminophenyl)-mercury was prepared via mercurisation of dimethylaniline with mercury(II) acetate followed by symmetrization with sodium thiosulfate [7,8]. Bis(*p*-anisyl)-mercury was prepared from *p*-bromoanisole and sodium amalgam [9]. Dibenzylmercury was obtained via symmetryzation of benzylmercury chloride [10] previously prepared from the Grignard reagent [11]. The synthesis of bis(*p*-carbomethoxy)phenyl)mercury was performed by Nesmeyanov's method [12].

Solvents

CCl_4 was refluxed for 18 hours over P_2O_5 and then distilled. $CHCl_3$ was dried for 3 days over anhydrous $CaCl_2$ and distilled over P_2O_5.

Interaction of XeF_2 with mercury(II) halides

1) 2.26 g (5 mmol) of HgI_2 and 0.845 g (5 mmol) of XeF_2 were placed into a nickel reactor. After stirring of the reagents a violent explosion occurred and evolution of I_2 was observed. The yield of HgF_2 was 1.1 g (92%). The structure of the solid product was confirmed by X-ray powder analysis (DRON-1.5 diffractometer; CuK_α radiation; Ni filter; cubic lattice, $a_0 = 5.53$ A).

2) 1.15 g (7 mmol) of XeF_2 and 40 ml of CCl_4 were placed in a reaction flask supplied with a stirrer and reflux condenser, then 2.3 g (7 mmol) of $HgBr_2$ was added to the solution which was warmed in a water bath for 30 min. The solid precipitate formed was filtered off, washed with CCl_4, and 1.6 g of the solid product was obtained. With X-ray powder analysis it was proved to be a mixture of HgF_2:$HgBr_2$ (7:1).

3) 2.17 (8 mmol) of $HgCl_2$ and 1.69 g (10 mmol) of XeF_2 were placed in the nickel reactor, gradually warmed for 30 min up to 200°C, and then the reactor was cooled to room temperature and opened. The evolution of chlorine was ob-

served. A 95% yield of HgF_2 was obtained (confirmed by X-ray powder analysis).

Interaction of XeF_2 with organomercury compounds

General procedure. 5 mmols of R_2Hg in CCl_4 or $CHCl_3$ solutions were placed in a flask connected to a gas burette which was filled with xylene. After bubbling Ar through the solutions during 30 min they were cooled down to appropriate temperatures and 10 mmols of XeF_2 were added into the thoroughly stirred solutions. The amounts of Xe evolved were measured with the gas burette. When the reactions were over (Xe evolution stopped) solid precipitates were filtered, washed with appropriate solvents and analysed using mass-spectrometer and elemental analysis techniques. Other products were analysed by GC-MS, and are listed in Table 1.

1) Reaction of XeF_2 with $(PhC{\equiv}C)_2Hg$. 2.3 g (14 mmol) of XeF_2 was added to solution of 2.74 g (6.8 mmol) of $(PhC{\equiv}C)_2Hg$ in 30 ml of cold $CHCl_3$. The reaction began at —5°C. This temperature was maintained until the reaction was complete and, when the Xe evolution stopped, 2.75 g (13 mmol) of Et_4NBr was added. The white precipitate of $PhC{\equiv}CHgBr$ (0.6 g; 22%; Found: C 25.60; Calcd. for C_8H_5BrHg: C, 25.13%) was separated, the solvent partially removed in vaccuo and yellow solid, $PhC{\equiv}CHgF$ (0.53 g; 24%), was obtained. This is well soluble in acetone, CH_3CN, DMF, moderately so in dioxane, ethyl acetate, dichloroethane, and unsoluble in CCl_4, benzene, ether, and alcohol. The product was purified via reprecipitation from acetone by alcohol; it decomposes at 170—175°C without melting. Found: C 30.02; Calcd.: C, 29.97%. Other products were discovered using GC-MS techniques (Table 1).

2) Reaction of XeF_2 with $(p\text{-}Me_2NC_6H_4)_2Hg$. 3.2 g (18.9 mmol) of XeF_2 were added to a cold (—60°C) solution of R_2Hg (4.24 g; 9.6 mmol) in $CHCl_3$ (120 ml). The reaction began at —40°C, the solution became blue and a solid precipitate of RHgF (3.1 g; 85%) appeared (Found: C, 28.31. Calcd. for $C_8H_{10}FHgN$: C, 28.24%). The compound is soluble in CH_3CN and DMF and insoluble in $CHCl_3$, CCl_4, benzene, alcohol, ether. It was purified via precipitation from acetonitrile by ether; it decomposes at 160—165° without melting. Other products are listed in Table 1.

3) Reaction of XeF_2 with $(p\text{-}MeOC_6H_4)_2Hg$. 1.2 g (7 mmol) of XeF_2 was added to a cold (—20°C) solution of R_2Hg (1.45 g; 3.5 mmol) in CCl_4 (50 ml). The slow Xe evolution began at 5°C. The temperature was allowed to rise up to 20°C, the reaction mixture was stirred for 3 hours and then filtered. 0.8 g of solid was obtained, it is insoluble in CCl_4, $CHCl_3$, benzene, CH_3CN, alcohol and ether, practically insoluble in acetone and DMF and decomposes at 155—160°C without melting. The elemental analysis (Found: C 18.27. Calcd. for C_7H_7FHgO: C, 25.72%) suggests that the product is a mixture of $RHgF/HgF_2$ (6/4 wt./wt.). For the other reaction products see Table 1.

4) Reaction of XeF_2 with $(p\text{-}EtO_2CC_6H_4)_2Hg$. 1 g (6 mmol) of XeF_2 was added to a cold (—20°C) solution of R_2Hg (1.42 g; 2.8 mmol) in CCl_4 (60 ml). The first signs of the reaction appeared at 25°C. To accelerate the process the reaction mixture was warmed in a water bath up to 50°C for an hour. When the reaction was completed, 0.19 g of solid precipitate (insoluble in acetone, alcohol, ether, $CHCl_3$ and CCl_4) was obtained; it decomposes at 160°C without melting. The elemental analysis (Found: C, 16.92. calcd. for $C_9H_9FHgO_2$: C, 29.27%) suggests that the precipitate is a $RHgF/HgF_2$ mixture (1/1 wt./wt.). For the other reaction products see Table 1.

5) Reaction of XeF_2 with $(PhCH_2)_2Hg$. 1.3 g (7 mmol) of XeF_2 was added to a cold (—60°C) solution of R_2Hg (1.23 g; 3.3 mmol) in $CHCl_3$ (25 ml). The Xe evolution began at —45°C, and a white precipitate appeared which when being filtered darkened and decomposed. For the other products see Table 1.

References

1 J. Gibson and A. Janzen, Canad. J. Chem., 49 (1971) 2168.
2 E. Lin and R. Lagow, J. Amer. Chem. Soc., 98 (1976) 8270.
3 L.V. Gurvich, G.V. Karachevtsev, V.N. Kondratyev, Yu.A. Lebedev, V.A. Medvedev, V.K. Potapov and Yu.S. Hodeev, Energii Rasriva Khimicheskich Svyasei, Nauka, Moskva, 1974.
4 L. Brandsma, Preparative Acetylenic Chemistry, Elsevier, Amsterdam, 1971, p. 82; H. Viehe, R. Merenyi, J. Oth and P. Valange, Angew. Chem., 76 (1964) 888.
5 M. Shaw, H. Human and R. Filler, J. Amer. Chem. Soc., 92 (1970) 6498; M. Brown, M. Shaw and R. Filler, J. Org. Chem., 36 (1971) 2917.
6 J. Johnson and W. McEwen, J. Amer. Chem. Soc., 48 (1926) 469.
7 O. Dimroth, Chem. Ber., 35 (1902) 2038.
8 V.P. Chalov, Zh. Obshch. Khim., 18 (1948) 608.
9 A. Michaelis, Chem. Ber., 23 (1890) 2344.
10 J. Maynard, J. Amer. Chem. Soc., 54 (1932) 2118.
11 S. Hilbert and G. Gruttner, Chem. Ber., 48 (1915) 906.
12 A.N. Nesmeyanov and L.G. Makarova, Zh. Obshch. Khim., 1 (1931) 598.