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OXIDATIVE REACTIONS OF ORGANOMETALLIC COMPOUNDS. INTERACTION OF ORGANOMERCURIALS WITH NITRIC ACID OR NITRONIUM SALTS

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SUMMARY

The interaction of organomercury compounds of the type RHgX (where X=R or Br; R=Ar or Alk) with NO_2BF_4 has been studied in sulfolane. It is shown that the reaction is a redox process leading when R=Ar to ArH as the principal product together with some $ArNO_2$. The main reaction path is governed by the escape of the Ar radical formed by a single-electron oxidation process from the reaction cage and its interaction with the solvent. In contrast, $ArNO_2$ is the main product of the reaction with nitric acid in Ac_2O. An attempt has been made to explain this difference in behaviour. Some RBr is formed when X=Br, indicating that the subsequent route of the oxidation process is very dependent on the decomposition path of the cation radical $(RHgX)^{+\cdot}$. When R=Alk a nitroalkane is one of the main reaction products whereas escape of the radical from the reaction cage leads not only to a hydrocarbon but also, through reaction of the radical with oxygen, to the formation of an aldehyde.

Many organometallic reactions traditionally referred to as electrophilic substitutions in fact proceed via a single-electron mechanism. The radicals initially formed are capable of coupling in the reaction cage to give "electrophilic substitution" products. That these reactions are radical processes is supported by the fact that the electrophilic substitution products formed are usually accompanied by radical products associated with the escape of radicals from the reaction cage[1,2], or alternatively that direct detection of radicals is possible via EPR spectroscopy[2] or that the reaction products exhibit dynamic nuclear polarisation[3,4]. It is, of course, always possible that an alternative mechanism exists, and that the reaction follows two routes simultaneously.

Electrophiles which are incapable of forming stable compounds during the course of the reaction generally yield radical decomposition products. An example is the action of transition metal salts on organometallic compounds, the transition metal being in its highest oxidation state[5]. The process is best explained in terms of a single electron transfer mechanism although a two-step reaction is possible involving

TABLE 1

RELATIVE YIELDS OF THE PRODUCTS FORMED FROM VARIOUS ORGANOMERCURY COMPOUNDS IN THE PRESENCE OF NO_2BF_4 IN TETRAMETHYLENESULFONE (TMS) AT 20°

No.	*Organo-mercury compound*	*Reagents ratio*	*Products, relative yields*	*Comment*
1	Ph_2Hg	1/1	$PhNO_2/PhH$, 1/1[a]	Tars formed
2	Ph_2Hg	1/1/1; Bu_4NBr added	$PhNO_2/PhH/PhBr$, 1/1/0.4	Traces of tars present
3	PhHgBr	1/1	$PhNO_2/PhH/PhBr$, 2.7/1/0.7	Tars formed
4	PhHgBr	1/1/1; Bu_4NBr added	$PhNO_2/PhH/PhBr$, 2.5/1/6.3	
5	PhHgOAc	1/1	$PhNO_2$	Same result obtained regardless of the order in which reagents mixed
6	PhHgBr	1/1; NO_2BF_4 in HF, LiF	$PhNO_2/PhH$, 1.7/1	PhF absent, *cf.* ref. 11
7	$(m\text{-}CH_3C_6H_4)_2Hg$	1/1	$PhCH_3$, *o*-, *m*-, *p*-NT, 40/1[b]	Insignificant amount of tars formed, the yield being quantitative with respect to NO_2BF_4
8	$(m\text{-}CH_3C_6H_4)_2Hg$	1/1/1; Bu_4NBr added	$PhCH_3$, *o*-, *m*-, *p*-NT, $m\text{-}CH_3C_6H_4Br$; 10/1/0.6[c]	Yield 90% with respect to NO_2BF_4
9	$(m\text{-}CH_3C_6H_4)_2Hg$	1/1; NO_2OAc	$PhCH_3$, *o*-, *m*-, *p*-NT; 16/1[b]	Yield 94% with respect to NO_2OAc
10	$m\text{-}CH_3C_6H_4HgBr$	1/1	$PhCH_3$, *o*-, *m*-, *p*-NT, $m\text{-}CH_3C_6H_4Br$, 1.5/1/0.6[c]	Yield 7% with respect to NO_2BF_4
11	$(m\text{-}BrC_6H_4)_2Hg$	1/1	PhBr, *o*-, *m*-, *p*-NBB, 13/1[d]	Same result, yield 48%
12	$(m\text{-}BrC_6H_4)_2Hg$	1/1/1; Bu_4NBr added	PhBr/*m*-NBB/ $m\text{-}BrC_6H_4Br$, 5/1/1.4	Same result, yield below 30%
13	$m\text{-}BrC_6H_4HgBr$	1/1	PhBr/*m*-NBB/ $m\text{-}BrC_6H_4Br$, 0.02/1/0.27	
14	Bu_2Hg	1/1/1; NaOAc added	$BuNO_2/BuOAc$, 29/1	Bu_2Hg dissolved in CH_2Cl_2 was added dropwise to solution of NO_2BF_4 and NaOAc in TMS; gas (probably butane) evolution observed
15	BuHgBr	1/1	$BuNO_2$/n-BuBr, 7/1	Traces of butyric aldehyde found
16	n-$C_7H_{15}HgBr$	1/1	$C_6H_{13}CHO/C_7H_{15}NO_2$/ n-$C_7H_{15}Br$, 10/3/1	

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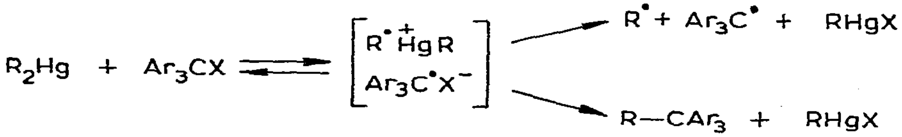
[a] $PhNO_2$ partially formed through the benzene nitration. [b] NT=nitrotoluene; the ratio given is that of the yield of toluene plus toluene nitration products to that of the *meta* isomer formed via route (I). [c] The ratio given is that of the yield of toluene plus toluene nitration products to that of the *meta* isomer formed via route (I) and $m\text{-}CH_3C_6H_4Br$. [d] NBB=nitrobromobenzene; the ratio given is that of the yield of bromobenzene plus bromobenzene nitration products to that of the *meta* isomer formed via route (I).

transmetallation followed by decomposition of the organometallic compounds formed (the latter step being undoubtedly an intramolecular redox process). If such reactions are regarded as redox processes it is possible to develop a general mechanism and to analyse cases in which the formation of "electrophilic substitution" products is accompanied by the production of "anomalous products"[6], the latter resulting from nucleophilic substitution reactions involving carbonium ions formed as a result of the further oxidation of the radicals present in the system. On the basis of this approach it follows that the percentage of the nucleophilic substitution products formed will increase as the oxidative properties of the electrophilic increase (see, for example ref. 7).

$$\mathrm{RM} \overset{-e}{\rightleftharpoons} [\mathrm{RM}]^{+\cdot} \longrightarrow \mathrm{R}^{\cdot} + \mathrm{M}^{+} \xrightarrow{-e} \mathrm{R}^{+} \xrightarrow{\mathrm{N}^{-}} \mathrm{RN}$$

The role of the nucleophile may be played by an anion which may be derived from the organometallic compound or the oxidising agent[6-10], by the solvent[6,8] or by an anion added to the system[11].

It has been shown recently[1,4] that organomercury compounds react with triphenylmethane derivatives (Ph_3CX) via an electron-transfer step, the composition of the products formed being dependent on the organomercury compound, the anion and the solvent. Only $(NO_2C_6H_4)_3C$ radicals are formed when tris(*p*-nitrophenyl)-methyl bromide is used[12].



Chemical polarisation of the protons was observed in the compound R–CAr_3.

In the present work, we have studied the interaction of some organomercury compounds with nitric acid or other oxidising agents such as nitronium tetrafluoroborate or chromic oxide.

Reactions with HNO_3 in acetic anhydride or with NO_2BF_4 in sulfolane (Tables 1 and 2) give, together with products arising from the nitration process, products due to other processes. The ratio of products formed is dependent on the nature of the oxidising agents and of the organomercury compounds. With unsymmetrical organomercurials, RHgBr, compounds such as RBr are also formed. Halogenated compounds have also been found amongst the products of the reaction of R_2Hg in the presence of the bromide ion. With alkylmercury compounds in acetic anhydride or in the presence of NaOAc, the reaction leads to the formation of ROAc. Blank experiments have demonstrated that such acetates do not arise as a result of solvolysis of the alkyl bromides formed in the reaction. It should also be noted that secondary isomers are formed in addition to primary bromides and acetates.

The formation of these various products may be explained in a variety of ways, depending on the route assumed for the decomposition of the organometallic cation-

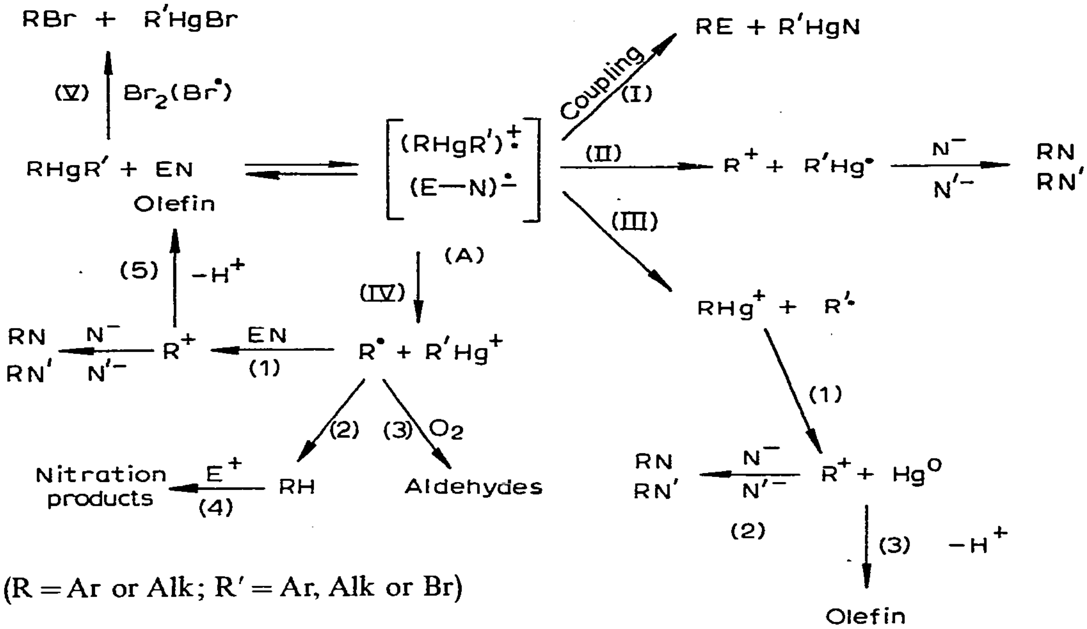
TABLE 2

RELATIVE YIELDS OF THE PRODUCTS FORMED FROM VARIOUS ORGANOMERCURY COMPOUNDS IN THE PRESENCE OF NITRIC ACID OR OTHER OXIDISING AGENTS AT 20°

No.	*Organo mercury compound*	*Oxidising agent, solvent*	*Conditions*	*Products, relative yields*	*Comment*
1	C_6H_5HgBr	HNO_3, Ac_2O	Two-fold excess of HNO_3	$PhNO_2/PhBr$, 7/3	This and the other reactions are heterogenous
2	m-BrC_6H_4HgBr	do.	Ten-fold excess of HNO_3	m-$NO_2C_6H_4Br$/ m-BrC_6H_4Br, 10/1	Total yield = 60%
3	m-$CH_3C_6H_4HgBr$	do.	Two-fold excess of HNO_3	m-$CH_3C_6H_4NO_2$, m-$CH_3C_6H_4Br$ (1–2%)	
4	o-$CH_3C_6H_4HgBr$	do.	do.	o-$CH_3C_6H_4NO_2$, p-$CH_3C_6H_4NO_2$ (5–10%), o-$CH_3C_6H_4Br$ (1–2%)	
5	p-$CH_3C_6H_4HgBr$	do.	do.	p-$CH_3C_6H_4NO_2$, p-$CH_3C_6H_4Br$ (1–2%)	
6	C_6H_5HgI	do.	do.	$PhNO_2/PhI$, 1/9	Small amounts of $O_2NC_6H_4I$ found
7	n-C_4H_9HgBr	do.	do.	n-BuOAc/s-BuOAc/n-BuBr/s-BuBr, 44/1/46/9	The yield of s-BuOAc is actually higher since hydrolysis occurred on neutralising the mixture. The reaction mixture became hot and the yield of secondary isomer increased when HNO_3 was added rapidly.
8	C_6H_5HgI	$CrO_3 \cdot 2Py$, CH_2Cl_2	Two-fold excess of oxidising agent	PhI	At room temperature the reaction proceeded slowly, the yield after an hour being 10–15%
9	$C_6H_5CH_2HgCl$	$CrO_3 \cdot 2Py$, CH_2Cl_2	Two-fold excess of oxidising agent	C_6H_5CHO/ $C_6H_5CH_2Cl$, 85/15	
10	C_6H_5HgI	CrO_3, $AcOH/Ac_2O$ (1/1)	One and a half excess of oxidising agent	PhI	Yield = 40%
11	$C_6H_5CH_2HgCl$	CrO_3, $AcOH/Ac_2O$(1/1)	One and a half excess of oxidising agent	C_6H_5CHO/ $C_6H_5CH_2Cl$, 95/5	C_6H_5CHO was not formed from $C_6H_5CH_2Cl$ under the conditions of the experiment
12	m-BrC_6H_4HgBr	Br_2, Ac_2O	Ten-fold excess of oxidising agent	$PhBr/m$-BrC_6H_4Br, 4/1	

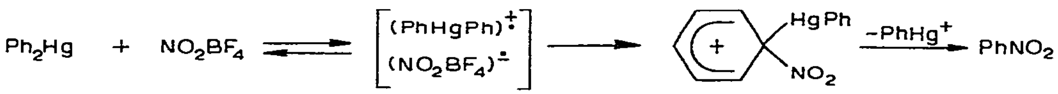
radical formed in the cage (A) during the oxidation of the organomercury compound with an electrophile.

The following reaction scheme includes the various possible decomposition routes in this process.



(R = Ar or Alk; R' = Ar, Alk or Br)

The interaction of ion-radicals in the cage may lead to the formation of electrophilic substitution products (route I) with the process probably proceeding via σ-complex formation in the case of arylmercury compounds.



Route (II) appears to be the least favourable. This is supported by the mass spectroscopy data obtained for organomercury compounds, in particular the appearance potentials observed for the various ions. Although these data only characterise the thermodynamic properties of cation-radicals in the gas phase, they may have some qualitative significance in solution also. Thus with CH_3HgCl and $(CH_3)_2Hg$, the appearance potentials for CH_3^+ [route (II)] were 14.8 and 13.4 eV, respectively, while for the cations HgCl and $HgCH_3$ [routes (III) and (IV)] they were 12.4 and 10.5 eV respectively[13]. Consequently, routes (IV) and (III) which lead to the formation of free radicals are preferred to route (II).

The results listed in Tables 1 and 2 demonstrate that organomercury compounds react with NO_2BF_4 in sulfolane mainly via a single-electron transfer process, which is followed by the movement of the radicals out of the cage [route (IV)]. Aromatic hydrocarbons from the escaped radicals may then be nitrated.

The nitro derivatives $ArNO_2$ may in fact be formed in two ways: (*a*) Through the coupling of $NO_2^{\cdot}$ directly in the cage with the radical cation at its radical site [route (I)]; note that the redox mechanism for electrophilic aromatic substitution has already been discussed[14]. (*b*) Through nitration of the ArH formed initially via route (IV). In fact, we have shown that the $ArNO_2$ formed in the process is mainly derived via a side nitration process involving the aromatic hydrocarbon.

Aromatic bromo derivatives which are formed in the reaction of NO_2BF_4 with Ph_2Hg in the presence of Bu_4NBr, or during the reaction with PhHgBr, may also arise in two ways: (*i*) through further oxidation of $Ph^{\cdot}$ radicals to the cation [route (IV)-(1)], or (*ii*) by direct bromination of the initial organomercurial [route (V)] by $Br^{\cdot}$ or Br_2 formed during the oxidation process [reaction (III)]. The formation of ArBr by the demercuration of $ArHgBF_4$ is less likely since arylmercury cations are known to be quite stable. In fact, both of the above mentioned processes probably occur since both Br^- and $R^{\cdot}$ are readily oxidised[15,16]. The experiments used in this study do not discriminate between these two processes. Thus, on the one hand, addition of bromide ions to the system involving PhHgBr increases the percentage of PhBr formed (run 4) and apparently supports the suggestion that bromodemercuration has occurred. In addition, ArOAc was not present amongst the products of the reaction of PhHgOAc with NO_2BF_4 nor was Ar_2Hg found in the presence of NO_2-OAc (run 9). On the other hand, however, the formation of tars is less pronounced when Ph_2Hg is reacted in the presence of Bu_4NBr (run 2) than in the absence of bromide ion. For this reason it is reasonable to assume that the cation formed in this system leads to the formation of PhBr in the first case, and enters into arylation or polyarylation reactions in the second case.

The reaction of alkylmercury derivatives (Bu_2Hg, BuHgBr, $C_7H_{15}HgBr$) with NO_2BF_4 in sulfolane also seems to lead to the formation of essentially radical products, since high percentages of hydrocarbons and aldehydes are formed in the reactions (runs 14–16). In addition, alkyl halides have also been shown to be present as well as nitro compounds which in this case must be formed via route (I).

In the presence of NaOAc, dibutylmercury gives butyl acetate amongst other products. As with aryl derivatives, the formation of AlkBr may arise either from the oxidation of radicals [route (IV)-(1)] or from the bromodemercuration of the initial organomercury compounds [route (V)], although the latter process occurs less readily with alkyl compounds than with aryl compounds. However, in reactions involving alkylmercury compounds, demercuration of the AlkHg cation leading to the formation of an alkyl cation which reacts with the bromide may make an important contribution to AlkBr formation. The same process may be responsible for the formation of the alkyl acetate (run 14), and hence the formation of the latter cannot be taken as evidence in support of a two-step oxidation mechanism [route (IV)-(1)].

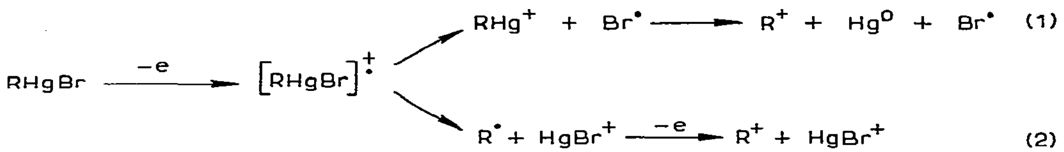
The alkyl cation may also be stabilised by elimination of a proton leading to the formation of an olefin [routes (III)-(3) and (IV)-(5)]. In the reaction of Bu_2Hg or BuHgBr with NO_2BF_4, hydride abstraction which also leads to olefin formation cannot be ruled out.

$$RCH_2CH_2HgX + NO_2Y \rightarrow RCH{=}CH_2 + HNO_2 + HgXY$$

In earlier studies alkylmercury derivatives have been shown to react with Ph_3CX to form triphenylmethane, the process occurring in several steps which include electron transfer from the organometallic compound to the Ph_3C cation followed by β-hydrogen abstraction[24].

Thus, halogenated derivatives may be formed by at least three different routes, *viz.*, (*a*) halodemercuration, (*b*) oxidation of radicals to carbonium ions and (*c*) demercuration of the RHg cation. The acetate may be formed via the latter two reactions.

If demercuration is considered to be an intramolecular redox process, there is no essential difference between the two-step paths (*b*) and (*c*) which lead to the formation of carbonium ions.



In fact, if the mercury metal formed in the reaction depicted in eqn. (1) is immediately oxidised to the Hg^{2+} cation, the two reactions will be comprised of two-step processes involving two electrons.

Quite different trends are observed in the reaction of ArHgBr with nitric acid in Ac_2O; unlike the reaction with NO_2BF_4, aromatic hydrocarbons are not formed, the products being solely $ArNO_2$ and ArBr. This behaviour may be linked with the fact that route (I), *i.e.* radical recombination in the cage, becomes the major pathway when the electrophilic properties of the reagent decrease. Under these conditions it may be assumed that only reaction (V) leads to the formation of ArBr, route (III)-(1,2) is less probable in this case, while route (IV) may not be involved at all since the presence of ArH has not been observed. The active reagent in the HNO_3/Ac_2O system is thought to be the mixed anhydride[17] rather than the nitronium ion. If NO_2BF_4 is replaced by NO_2OAc, the oxidative properties of the electrophile decrease. An earlier study of the reaction of organomercury compounds with triphenylmethane derivatives arrived at the conclusion that a decrease in the nucleophilic properties of the organomercury compound or in the electrophilic properties of Ph_3CX decreased the probability of the radicals leaving the cage; the present results agree with this conclusion.

With NO_2BF_4 or HNO_3 as the oxidant, the extent to which various pathways contribute to the overall mechanism may also depend on the nature of the solvent used, as well as on the reaction conditions. For example, the fate of the radicals leaving the cage may well depend on how effectively hydrogen abstraction competes with oxidation to the cation, the difference between the rates of these two processes being dependent on the solvent.

The relative percentage of radical recombination products to out-of-cage radical products is discussed below.

The halides formed during the reaction of organomercury compounds with nitric acid in acetic anhydride may arise via the same route as the products of the reaction with nitronium tetrafluoroborate. However, since aryl radicals leave the cage less readily in the presence of HNO_3 (see below), the aryl bromides are most probably formed via halodemercuration [route (V)]; this route appears to be most favoured for arylmercury iodides. Alternatively, it is necessary to assume that the radicals formed are completely oxidised to cations with the result that the reaction with the solvent which normally leads to the formation of ArH, does not in fact take place.

The existence of route (V), which involves participation of bromine, has been tested with *m*-BrC_6H_4HgBr (run 10, Table 2). The main product, however, turned out to be bromobenzene and not dibromobenzene (a possible alternative electrophilic bromination product). In the reaction with HNO_3, bromobenzene was absent to all intents and purposes. These results are in complete disagreement with the assumption that ArBr might be formed via route (V) with the involvement of either molecular bromine or the bromine radical.

It has been mentioned above that, unlike the reaction with NO_2BF_2 in sulfolane, organomercury compounds react with HNO_3 in Ac_2O to give nitro derivatives as the main reaction product, while the corresponding hydrocarbon, which might have been formed if the radical had escaped from the cage, is not present. It could be assumed that this behaviour may be attributed to the difference between the oxidative abilities of the electrophiles involved. Phenylmercury derivatives, however, are not suitable for resolving this problem as the benzene formed via route (IV)-(2) may be involved further in aromatic nitration thus influencing the real yield of the in-cage product. Indeed, a study of the composition of the product formed under various reaction conditions, (*i.e.*, in the presence of variable amounts of nitronium tetrafluoroborate added to Ph_2Hg or PhHgBr) has shown that the amount of benzene formed is greater initially than in the later stages of the reaction while the rate at which benzene is consumed is roughly equal to the increase in the yield of nitrobenzene.

The use of organomercury compounds containing *meta* substituents (CH_3 or Br) enables a completely unambiguous estimation of the ratio of nitration products arising from routes (I) and (IV). In fact, electrophilic substitution [route (I)] should lead to the formation of the respective *meta* derivative alone while subsequent nitration should lead to a mixture of isomers containing mainly *ortho* and *para* forms and having a fixed composition (*o*-/*m*-/*p*- 56.5/3.5/40 for $C_6H_5CH_3$; *o*-/*p*- 76/24 for C_6H_5Br[18]).

Symmetrical organomercury compounds such as $(m\text{-}YC_6H_4)_2Hg$ ($Y=CH_3$, Br) react with NO_2BF_4 to yield mainly substituted benzenes, YC_6H_5, together with smaller amounts of the subsequent nitration products; however, the yield of the *meta* isomers is greater than the value to be expected from mere nitration of the hydrocarbon ArH. Table 1 lists the ratios of the yield of ArH plus nitration products to that of the *meta* isomer formed via route (I); this gives a measure of the relative ratio of out-of-cage to in-cage processes in this system. The ratio appears to depend on the nature of the organomercury compound and increases on introduction of an electron donor substituent. This is similar to the trend observed during the reaction of Ar_2Hg with Ph_3CX[1,4].

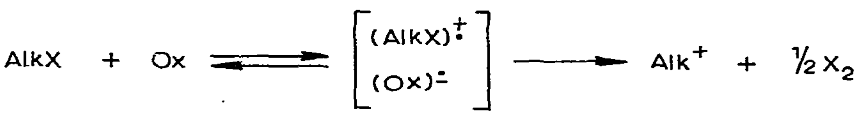
On replacing symmetrical organomercury compounds with unsymmetrical species, the percentage of recombination product ($m\text{-}YC_6H_4NO_2$; $Y=CH_3$, Br) formed increases steeply, especially in the case of the relatively less reactive *m*-bromophenylmercury bromide. It should be noted that the total yield of product decreases when R_2Hg is replaced by RHgBr or the *m*-tolyl derivative is replaced by the *m*-bromophenyl. Thus, the reaction is virtually quantitative with respect to nitronium tetrafluoroborate with $(m\text{-}CH_3C_6H_4)_2Hg$ whereas the yield is merely 20 to 30% with the unsymmetrical organomercury compound. Since these reactions are of purely theoretical significance no attempt has been made to achieve optimal conditions as far as product yields are concerned; for this reason only relative yields are listed in the Tables.

It has already been mentioned that the ratio YC_6H_5/m-$YC_6H_4NO_2$ decreases as the electrophilic properties of the nitrating agent decrease; thus, the reaction with NO_2BF_4 in the presence of Bu_4NBr (runs 4, 8 and 12), in which NO_2Br may be formed, leads to a decrease in the relative yields of the out-of-cage products. On the other hand, the yield of toluene is quite significant even in the reaction involving NO_2OAc (run 9; however, a symmetrical organomercury compound is the substrate here) although the out-of-cage/in-cage ratio is 16 in this case, in comparison with the value of 40 found when acetate is absent.

The same factors probably lead to the formation of the in-cage compound as the principal product in the reaction of substituted phenylmercury bromides with HNO_3 in Ac_2O. In this case, (Table 2, runs 2 and 3), hardly anything other than the respective *meta* isomers (*m*-nitrotoluene and *m*-nitrobenzene) is formed. With *p*- or *o*-tolylmercury bromides, only one of the isomers, *p*- or *o*-nitrotoluene, is formed respectively.

The results discussed above lead to the conclusion that in the systems studied the reaction of organomercury compounds with nitrating agents proceeds via a redox mechanism, this conclusion being supported by the formation of radical products. A natural assumption is that the mechanism is also valid for similar reactions involving other organometallic compounds, *e.g.*, organotin compounds. To test this assumption, the reaction of tetraphenyltin with NO_2BF_4 in sulfolane has been studied and it has been shown that in this case also benzene is formed together with nitrobenzene ($PhNO_2/PhH$ 1/2).

To increase the product yields, especially in the reaction with RHgBr, it is possible to use higher concentrations of the oxidising agent. Excess nitronium tetrafluoroborate has not been used, however in order to avoid the possible reaction of the alkyl halides formed with NO_2BF_4, and thus avoid a reaction which may, in principle, also be a redox process. This reaction is known to give nucleophilic substitution products such as the nitrate[19] and alkyl-cation/solvent interaction products[10] in addition to products arising from interactions involving a specially added nucleophile; in fact fluoroalkanes have been synthesised via the latter method[21]. An S_N1 heterolytic mechanism has been assumed for this reaction[19b] although a redox mechanism would be equally acceptable and would agree with the observed tendencies which follow the series iodides > bromides > chlorides.

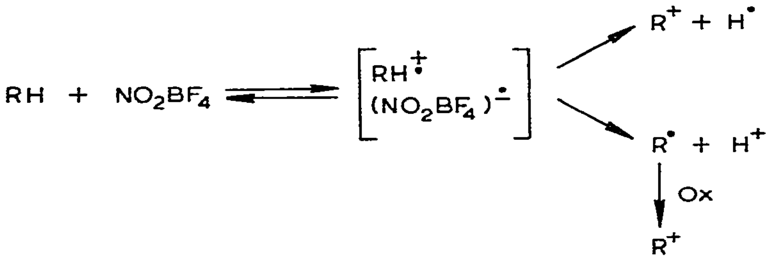


$$\text{AlkX} + \text{Ox} \rightleftharpoons \left[\begin{matrix}(\text{AlkX})^{+\cdot}\\(\text{Ox})^{-\cdot}\end{matrix}\right] \longrightarrow \text{Alk}^+ + \tfrac{1}{2}X_2$$

In the present study, the presence of alkyl cations has been established through the formation of cumene in the reaction of isopropyl iodide with nitronium tetrafluoroborate in sulfolane containing benzene; the main product in this reaction was, of course, nitrobenzene.

It is interesting to speculate whether a redox mechanism is also valid for the reactions of alkyl halides with halogens, *e.g.*, AlkI with Cl_2 or ICl, the reactions which reportedly proceed via a classical heterolytic mechanism[22].

It is not possible to entirely rule out the assumption that the nitration of alkanes with NO_2BF_4[23] also proceeds via a one-step (or a consecutive two-step) electron transfer.



In fact, the scheme readily accounts for all the products formed. We have found that heptane, heptyl iodide, or heptene also form the same product mixtures, although the product ratios are different. Unfortunately, decomposition occurs to a noticeable extent during the course of this reaction (in agreement with the fact that nitromethane is formed from ethane and NO_2BF_4[23]) and a large variety of products is formed.

In addition to HNO_3 and NO_2BF_4, chromic oxide in acetic acid plus acetic anhydride or in the form of a complex with pyridine in methylene chloride has also been used for the oxidation of organomercury compounds. With phenylmercury iodide, both of these oxidants give iodobenzene as the sole product. The reaction is very rapid in $AcOH/Ac_2O$ (1/1) and gives PhI quantitatively (see Table 2). Oxidation of diphenylmercury under these conditions gives phenyl acetate. It is possible that the latter compound may have been formed via the oxidation of benzene, and for this reason blank experiments have been carried out showing that only a very small percentage of benzene is oxidised to phenyl acetate during the time taken to complete the reaction with Ph_2Hg. Under the same conditions benzylmercury chloride is oxidised to benzyl chloride and benzaldehyde; hence the benzyl radical, unlike the phenyl radical, is not only oxidised by CrO_3 to the benzyl cation but also reacts with atmospheric oxygen. Special experiments have shown that benzyl chloride is virtually unaffected by chromic oxide under these reaction conditions and over the time period necessary for the reaction.

EXPERIMENTAL

Reagents and solvents

Tetramethylenesulfone (sulfolane, TMS, "Merk for synthesis" purity grade) was stored over 4A molecular sieves, treated with calcium hydride at 60° for 6h and distilled *in vacuo* over fresh calcium hydride.

Acetic anhydride and glacial acetic acid ("pure for analysis" purity grade) were distilled before use. Nitric acid (*d* 1.37 to 1.38, 59 to 60%) was used unchanged.

Methylene chloride ("pure for analysis" purity grade) was treated with conc. sulfuric acid, washed with aqueous sodium bicarbonate, dried over calcium chloride and distilled.

Nitronium tetrafluoroborate was synthesised from nitric acid, hydrogen fluoride and boron trifluoride in methylene chloride[25].

The various alkyl iodides employed were treated to remove iodine before use and then distilled.

Organomercury compounds were synthesised using known procedures[26]. The melting points obtained agreed with those reported in the literature. Bis(*m*-bromophenyl)mercury was prepared by a similar method to that used in the preparation of bis(*p*-bromophenyl)mercury[26]; m.p. 163–164 (from acetone). The corresponding unsymmetrical compound was synthesised from R_2Hg and mercury dibromide; m.p. 210–212° (from acetone). 1-Nitroheptane used as the chromatographic standard was prepared as described previously[27]. The complex $CrO_3 \cdot 2$ Py was synthesised using the method described in ref. 28.

GLC analysis

The columns used and the conditions employed are listed below:

(1). Chromosorb W, 60 to 80 mesh; 16% Apiezon L; length 1.5 m, dia. 4 mm; column temp., 80 or 130°; nitrogen flow rate, 48 ml/min.

(2). Chromosorb W, 60 to 80 mesh; 20% SE-80; length 1.5 m, dia. 4 mm; column temp., 80°; helium flow rate, 65 ml/min.

(3). Chromosorb G, 60 to 80 mesh; 5% PEG-6000; length 0.9 m, dia. 4 mm; column temp., 170° helium flow rate, 66 ml/min.

(4). Gas-Chrom, 20% SE-30; length 1.5 m, dia. 4 mm; column temp., 120 to 160°; helium flow rate, 65 ml/min.

(5). Gas-Chrom, 3% NGA; length 1.5 m, dia. 4 mm; column temp., 80 or 130°; helium flow rate, 46 ml/min.

Columns 1, 2 and 5 were used for mixtures of primary and secondary butyl bromides with butyl acetate or for benzene/bromobenzene/nitrobenzene mixtures. Nitrotoluenes were analysed on columns 1 and 4, while nitrobromobenzenes were analysed on column 3.

Interaction of NO_2BF_4 with various substrates in sulfolane or anhydrous hydrogen fluoride

The reactions of nitronium tetrafluoroborate with organomercury compounds in sulfolane were carried out as follows. Nitronium tetrafluoroborate (1 ml of a 0.7 *M* solution in TMS) was added over a period of 6 min to a solution of the substrate (7×10^{-4} mol in 2 ml TMS) in a reaction vessel fitted with a magnetic stirrer. After 30 min, the mixture was diluted with 10 ml water and the solution of the chromatographic standard added. The mixture was filtered (if necessary), then treated with sodium bicarbonate and extracted with 2 ml portions of pentane (sometimes ether) 5–6 times. The combined extracts were dried over 4A molecular sieves and analysed using GLC methods.

The reactions in anhydrous hydrogen fluoride were conducted as follows. A sample of NO_2BF_4 dissolved in 10 ml HF was added slowly to a substrate dissolved in a solution of anhydrous LiF in HF. The reaction temperature was maintained at about +15°. After addition of nitronium tetrafluoroborate had been completed, the reaction mixture was stirred with a magnetic stirrer for a further hour and poured into ice cooled with liquid nitrogen. The mixture was treated with sodium bicarbonate until evolution of carbon dioxide had ceased and then extracted with ether three times. The combined extracts were dried over anhydrous magnesium sulfate and analysed using GLC methods. In some experiments, NO_2BF_4 in TMS was added to the solution of the substrate in anhydrous HF when pentane was used as the extractant.

Interaction of NO_2BF_4 with isopropyl iodide in TMS containing benzene

NO_2BF_4 (2 ml of a 0.7 *M* solution) was added slowly to a vigorously stirred solution of benzene (7×10^{-4} mol) and isopropyl iodide (2.8×10^{-3} mol) in 4 ml of TMS contained in a flask fitted with a magnetic stirrer. The mixture was worked up in the usual way, GLC analysis being performed on column 1 at 80°. The yield of cumene was 1.8% while that of nitrobenzene was 92%.

Interaction of organomercury compounds with nitric acid in acetic anhydride

Conc. nitric acid (1 ml) was added dropwise to the substrate (0.001 mol) in Ac_2O. The reaction mixture was vigorously stirred and well cooled (so that the reaction temperature did not exceed 28°). The mixture was stirred at room temperature for a further hour, poured into 100 ml water and neutralised with sodium bicarbonate. The aqueous solution was filtered, extracted with two 30 ml portions of ether, the combined extracts dried over anhydrous magnesium sulfate and the ether evaporated to give 8 ml of the residue which was analysed using GLC methods. In some cases treatment of the reaction mixture influenced the product ratio. In these cases the initial mixture was analysed.

Interaction of organomercury compounds with $CrO_3 \cdot 2$ Py in methylene chloride

The substrate (0.001 mol) was added to $CrO_3 \cdot 2$ Py (ca. 0.07 g) dissolved in 10 ml methylene chloride. The mixture was shaken for an hour, poured into 50 ml water and the upper layer washed with dilute hydrochloric acid and with dilute sodium bicarbonate. The solution was dried over anhydrous magnesium sulfate, evaporated, and analysed using GLC methods.

Interaction of organomercury compounds with chromic oxide

CrO_3 (0.11 g) was gradually added to the substrate (0.001 mol) dissolved in 3 ml of an $AcOH/Ac_2O$ (1/1) mixture. The reaction mixture was shaken for an hour and cooled, then poured into 50 ml water, neutralised with sodium bicarbonate, extracted with ether, dried over magnesium sulfate and analysed using GLC methods.

The attempted acetolysis of n-butyl bromide under the above reaction conditions

n-BuBr (0.01 mol) and $HgBr_2$ (0.005 mol) were dissolved in 5 ml of an $AcOH/Ac_2O$ (1/1) mixture. The reaction mixture was stored for 48 h. No n-butyl acetate was found when the solution was subsequently analysed by GLC methods using column 2.

Interaction of (m-bromophenyl)mercury bromide with bromine in acetic anhydride

Bromine (0.01 mol in 2 ml Ac_2O) was added to (*m*-bromophenyl)mercury bromide (0.001 mol in 4 ml Ac_2O). The bromide dissolved completely. The mixture was worked up in the usual way, GLC analysis being performed on column 3.

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Note added in proof. While this manuscript was in preparation a paper was published (C. Eaborn, Z. C. Salih, D. R. M. Walton, *J. Chem. Soc., Perkin II*, (1972) 172) in which Si–C bond cleavage in aryltrimethylsilanes under the action of nitric acid in acetic anhydride was reported to proceed via nitrosodesylilation followed by the oxidation of the nitroso to nitro derivatives. A mechanism of this type may also be possible in the reaction of diarylmercury compounds with nitric acid. The differences observed between the reactions with NO_2BF_4 in sulfolane and with HNO_3 in Ac_2O might be explained on the basis of this mechanism.