Reaction of Arylmercuric Chlorides with Sodium Naphthalenide†

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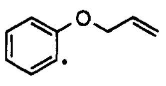
Reactions of sodium naphthalenide ($Na^+Np^{\bullet-}$) with arylmercuric chlorides, ArHgCl, Ar = phenyl (**1a**), *o*-anisyl (**1b**), *p*-anisyl (**1c**), *p*-tolyl (**1d**), *p*-nitrophenyl (**1e**), and *o*-(allyloxy)phenyl (**1f**), were carried out. The products were mainly diarylmercurials (Ar_2Hg, **3**) and smaller amounts of arene (ArH, **2**). The yield of **3** was smaller and the yield of **2** greater when reactant ratios $Np^{\bullet-}$/ArHgCl were 2:1 rather than 1:1, resulting, it is proposed, from further reaction of Ar_2Hg with the excessive amount of $Np^{\bullet-}$. Reactions of $Np^{\bullet-}$ with **3b–d** gave quantitative yields of **2b–d**. Reaction of **1f** with $Np^{\bullet-}$ gave not only **2f** and **3f** (mainly) but also small amounts of 3-methyl-2,3-dihydrobenzofuran (**7**), attributable to formation and cyclization of the *o*-(allyloxy)phenyl radical in a minor reaction pathway, and phenol (**8**), attributable to reaction of first-formed **2f** with $Np^{\bullet-}$. Reaction of $Np^{\bullet-}$ with allyl 2-bromophenyl ether (**9**) in 1:1 and 2:1 ratios gave analogous results, namely **2f** (mainly), **7**, and **8**. The results do not support an aryl radical ($Ar^\bullet$) route in conversions of ArHgCl to Ar_2Hg, but one in which the Ar–Hg bond is not broken. Good material balances were obtained with all reactions except that with **1e**.

Introduction

The reaction of organomercuric chlorides, RHgCl, with reducing agents can take two major routes. Either reduction, to RH, or symmetrization, to R_2Hg, can occur, depending, especially, on the nature of R. A number of publications on this subject have appeared in recent years, concerned particularly with whether reaction leads to the free radical $R^\bullet$, from which the products are derived.

Russell and co-workers found evidence for radical formation in reactions of a number of alkylmercuric chlorides with salts of secondary and tertiary nitroalkanes under photostimulation.[1] Particularly important was the finding that when 1-(chloromercurio)-5-hexene was used with the anion of 2-nitropropane, 2-(cyclopentylmethyl)-2-nitropropane was formed, indicating that photostimulated electron transfer to 1-(chloromercurio)-5-hexene must have generated the rapidly cyclizing 5-hexenyl radical. In contrast with that result, however, analogous evidence could not be found for the formation of the 2-(allyloxy)phenyl radical (**4**) when [2-(allyloxy)phenyl]mercuric chloride (**1f**), was used. The radical **4** is well-known to cyclize to the 3-(2,3-dihydrobenzofuryl)methyl radical (**5**) very rapidly ($k = 6.3 \times 10^9$ s^{-1} at 30 °C[2]). Had **4** ($R^\bullet$) been formed in the reaction of **1f**, the cyclized radical **5** ($R'^\bullet$) should have been formed and trapped as $Me_2C(R')NO_2$, in analogy with the 5-hexenyl case. None of the trapping product was obtained, however. Instead, 17% of the symmetrization product, Ar_2Hg (**3f**), was obtained, in which Ar was uncylized 2-(allyloxy)phenyl. Russell attributed symmetrization not to photostimulated reduction of **1f** itself, but of $HgCl_2$, complexed with 2-nitropropanate ion, and existing in an equilibrium (eq 1) which ordinarily lies far to the left.



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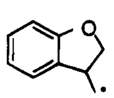

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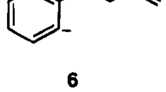

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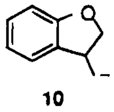

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$$2ArHgCl \rightleftharpoons Ar_2Hg + HgCl_2 \qquad (1)$$

Russell found, furthermore, that whereas added di-*tert*-butyl nitroxide prevented the trapping of alkyl radicals (e.g., benzyl, isopropyl) by 2-nitropropanate, it had no effect on the symmetrization reaction of **1f**, corroborating thereby, that the radical **4** was not involved. Singh and Khanna,[3] on the other hand, found that reaction of sodium naphthalenide with benzyl-, phenyl- (**1a**), *p*-tolyl- (**1d**), and (*p*-nitrophenyl)mercuric chloride (**1e**) in THF led not only to symmetrization but also to formation of the corresponding arene and small amounts of biaryl. On the basis of these results and their finding that added cumene enhanced toluene formation but inhibited symmetrization and bibenzyl formation from benzylmercuric chloride, Singh and Khanna attributed reactions of all of their organomercuric chlorides to the initial formation of radicals. The symmetrization reaction was represented, then, with eq 2. The effect of added cumene on reactions of the arylmercuric chlorides was not reported.

$$R^\bullet + RHgCl \rightleftharpoons [R_2HgCl]^\bullet \xrightarrow{e^-} [R_2HgCl]^- \rightleftharpoons R_2Hg + Cl^- \qquad (2)$$

Quantitative symmetrization was achieved by Todhunter and Currell[4] in the reduction of *p*-(chloromercurio)benzoic acid (**1g**) with dithionite in ethanol solution. In this case, direct two-electron reduction of **1g** was pro-

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† Dedicated to Professor Glen A. Russell on the occasion of his 70th birthday.

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(1) Russell, G. A.; Hershberger, J.; Owens, K. *J. Organomet. Chem.* **1982**, *225*, 43.

(2) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594.

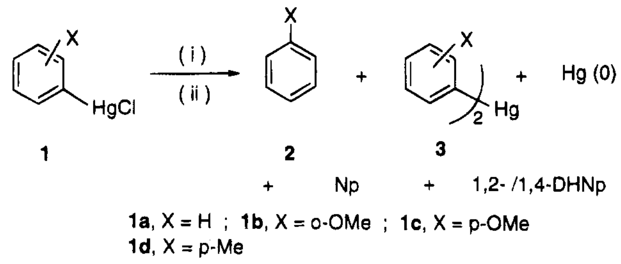
(3) Singh, P. R.; Khanna, R. K. *Tetrahedron Lett.* **1983**, 973.

(4) Todhunter, J. A.; Currell, D. L. *J. Org. Chem.* **1975**, *40*, 1362.

(5) Beckwith, A. L. J.; Meijs, G. F. *J. Chem. Soc., Chem. Commun.* **1981**, 136,

0022-3263/95/1960-5414$09.00/0

Scheme 1[a]



[a] Key: (i) $Na^+Np^{\bullet-}$ in THF; (ii) H_2O, workup.

posed, and symmetrization was attributed to reaction of $ArHg^-$ with ArHgCl (eqs 3–5).

$$ArHgCl + 2e^- \rightarrow ArHg^- + Cl^- \quad (3)$$

$$ArHg^- + ArHgCl \rightarrow ArHgHgAr + Cl^- \quad (4)$$

$$ArHgHgAr \rightarrow Ar_2Hg + Hg \quad (5)$$

Connected with the search for radicals in reductions of arylmercuric halides are reductions of aryl halides themselves, and again the 2-(allyloxy)phenyl probe has had an important role. Beckwith and Meijs[5] reported that reaction of allyl 2-iodophenyl ether with sodium naphthalenide in THF gave allyl phenyl ether (**2f**) and 3-methyl-2,3-dihydrobenzofuran (**7**) in 14% and 3% yields, respectively. Reaction with $Cr(II)en_2(ClO_4)_2$ also gave mostly **2f** (69%) and only 16% of **7**. They noted, therefore, that a second reduction of **4** to the 2-(allyloxy)phenyl anion (**6**) clearly competed effectively with cyclization.

Similarly, Sawaki and co-workers[6] reported that cathodic reduction of allyl 2-chlorophenyl ether gave either none or very little of **7**, but mainly **2f**, phenyl (*Z*)-propenyl ether, and 2-chlorophenyl (*Z*)-propenyl ether, from which it was concluded that **4**, formed at the cathode, must be reduced to **6** with a rate constant over 10^{10} s^{-1}.[6] This conclusion, that reduction of the probe radical is faster than cyclization, is similar to that reached by Garst for the 5-hexenyl radical in reactions of 5-hexenyl 1-halides with sodium naphthalenide.[7]

In continuing our search for aryl radical formation in electron transfer reactions with arylmercurials,[8–11] we have made a new study of the products of reaction of **1f** with sodium naphthalenide. For comparison we have made a similar study with phenyl- (**1a**), *o*-anisyl- (**1b**), *p*-anisyl- (**1c**), *p*-tolyl- (**1d**), and (*p*-nitrophenyl)mercuric chloride (**1e**) and with allyl 2-bromophenyl ether (**9**).

Our results, more quantitative than those hitherto published, provide further understanding of these reactions.

Results and Discussion

Reactions of 1a–d with $Np^{\bullet-}$. These reactions (Scheme 1) led mainly to symmetrization (**3a–d**) but also to substantial amounts of arene (**2a–d**). Naphthalene (Np) and both 1,2- and 1,4-dihydronaphthalene (DHNp) were formed and were assayed along with products **2** and **3** by GC. Metallic mercury (Hg) was isolated and weighed. Reaction with **1e** ($X = p\text{-}NO_2$) was carried out, but, as found also by Singh and Khanna,[3] was not quantitative, and is not reported.

Table 1. Products of Reaction of Arylmercuric Chlorides (RC_6H_4HgCl, 1a–d) with Sodium Naphthalenide ($Np^{\bullet-}$)[a]

		mmol × 10^2		products, mmol × 10^2 and %[b]				
run	R	**1**	$Np^{\bullet-}$	**2**[c]	**3**[d]	Hg	Np[e]	**1**[f]
1	H, **1a**	72	72	12 17[g]	27 77[g]	38	67 93	1.7
2	H, **1a**	32	65	12 38[h]	9 56	21	59 91	
3	*o*-OMe, **1b**	37	36	1.1 3.0[g]	16 89[g]	17	33 92	1.0
4	*o*-OMe, **1b**	9.8	20	3.1 32	3.5 71	5.1	19 95	
5	*p*-OMe, **1c**	13	12	1.3 12	4.5 85	5.5	11 92	2.4
6	*p*-OMe, **1c**	20	40	5.3 27	7.3 73	11	38 95	
7	*p*-Me, **1d**	15	15	1.2 8.8	6.1 90	6.2	14 93	1.4
8	*p*-Me, **1d**	9.9	20	1.1 11	4.4 89	4.2	18 90	

[a] In THF at room temperature. Solution of **1** added to solution of $Np^{\bullet-}$ in runs 2, 4, 6, and 8; solution of $Np^{\bullet-}$ added to solution of **1** in runs 1, 3, 5, and 7. [b] Second entry in each run. Yields from **1** based on Ar group content. [c] Benzene, anisole, and toluene, as appropriate. [d] Ar_2Hg, as appropriate. [e] Sum of Np, 1,2- and 1,4-DHNp. [f] Recovered. [g] After compensating for unused **1**. [h] Approximately 0.001 mmol (0.6%) of biphenyl was also obtained.

The stoichiometry of symmetrization requires a 1:1 ratio of $Np^{\bullet-}$ and ArHgCl (eq 6). Bearing this and the

$$2ArHgCl + 2Np^{\bullet-} \rightarrow Ar_2Hg + Hg + 2Np + 2Cl^- \quad (6)$$

report by Singh and Khanna[3] in mind that reactions were not complete unless a 2:1 ratio of $Np^{\bullet-}$/ArHgCl was used, we carried out reactions with both ratios of reactants. It is seen in Table 1 with **1a–d** (runs 1, 3, 5, 7) that at a 1:1 ratio the major product was **3** (Ar_2Hg, 77–90%), from symmetrization. Arene **2** (ArH) was also formed, and a small amount of ArHgCl was recovered in each case. In contrast, at the 2:1 ratio (runs 2, 4, 6, 8), the amount of Ar_2Hg decreased and the amount of arene increased. We attribute this difference to the reaction of Ar_2Hg itself with $Np^{\bullet-}$. Singh and Khanna noted that the diarylmercurials reacted with $Np^{\bullet-}$ but more slowly than the arylmercuric chlorides.[3] We found, in fact, with **3b–d**, that reaction gave the corresponding arenes quantitatively (Table 3) with the stoichiometric ratio $Np^{\bullet-}$/**3** of 2:1. This is shown in eq 7, where SH denotes protonation

$$Ar_2Hg + 2Np^{\bullet-} \xrightarrow{SH} 2ArH + Hg + 2Np \quad (7)$$

of Ar^- by solvent THF. We chose the protonation route to arene rather than a free radical route with $Ar^\bullet$ on the basis of our results with **1f**, discussed later. Insofar as protonation by THF is concerned, the pK_a of THF in DMSO has been estimated to be 35[12] and the pK_a of benzene estimated, from exchange with cyclohexylamide,

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(6) Kimura, M.; Miyahara, H.; Moritani, N.; Sawaki, Y. *J. Org. Chem.* **1990**, *55*, 3897.

(7) Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400.

(8) Rhodes, C. J.; Agirbas, H.; Shine, H. J.; Hoque, A. K. M. M.; Venkatachalam, T. K. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2129.

(9) Hoque, A. K. M. M.; Shine, H. J.; Venkatachalam, T. K. *Collect. Czech. Chem. Commun.* **1993**, *58*, 82.

(10) Lochynski, S.; Hoque, A. K. M. M.; Shin, S. R.; Shine, H. J. *Magn. Res. Chem.* **1991**, *29*, 282.

(11) Lochynski, S.; Shine, H. J.; Soroka, M.; Venkatachalam, T. K. *J. Org. Chem.* **1990**, *55*, 2702.

(12) Private comunication from Prof. Fred Bordwell.

Table 2. Products of Reaction of [2-(Allyloxy)phenyl]mercuric Chloride (1f) with Sodium Naphthalenide ($Np^{\bullet-}$)[a]

	mmol × 10^2		products, mmol × 10^2 and %[b]						ratio[c]	
run	**1**[f]	$Np^{\bullet-}$	**2f**	**3f**	**7**	**8**[c]	Hg	Np[d]	(**2f** + **8**)/**7**	**2f**/**8**
9[e]	16[f]	16	0.50	7.3	0.10	0.09	8.0	15	5.9	5.5
			3.1	91	0.62	0.56	50	94		
10[e]	5.1	10	0.44	2.1	0.19	0.23	2.5	9.2	3.5	1.9
			8.6	82	3.7	4.0	49	92.0		
11[g]	5.2	10	0.15	2.2	0.15	0.37	2.5	9.4	3.5	0.41
			2.9	85	2.9	7.1	48	94		

[a] In THF at room temperature. In run 9 each reactant was dissolved in 2.5 mL of THF; in runs 10 and 11, 5 mL each was used. [b] Second entry in each run. Yields from **1f** are based on Ar group content. [c] Included in the amount of **8** is the small amount of the unidentified products, *m/e* 134, believed to have been formed from **2f** in its reaction with $Np^{\bullet-}$. [d] Sum of Np, 1,2- and 1,4-DHNp in overlapping GC peaks. [e] Solution of $Np^{\bullet-}$ added to solution of **1f**. [f] After compensating for 0.53 × 10^{-2} mmol recovered. [g] Solution of **1f** added to solution of $Np^{\bullet-}$.

to be 43.[13] These data indicate that protonation of aryl anions by THF should be facile.

When **1** is added to a solution of $Np^{\bullet-}$, therefore, two major reactions can occur. The first of these appears to be symmetrization (Ar_2Hg), and the second is reduction of the Ar_2Hg. Reduction of **1** itself to the aryl radical stage may, in fact, be a minor pathway.

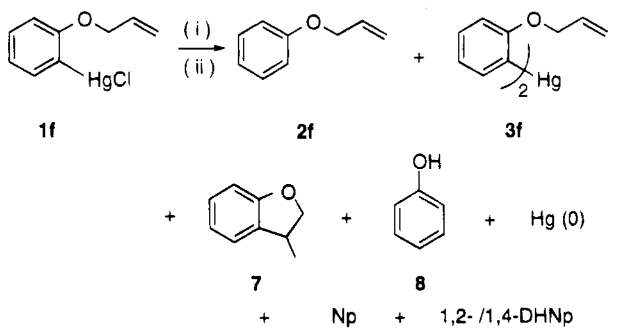
The two reactions, symmetrization and arene formation, have different stoichiometries, and these stoichiometries are independent of mechanism. We have applied the stoichiometries to our data in Table 1, assuming that all of the **1** that reacted was first symmetrized (product **3**) and that some of the **3** was next reduced to arene **2**. With this approach we obtain a reasonable accounting of reactants and products for the 1:1 reactions. On the other hand, the accounting for the 2:1 reactions shows that an excess of $Np^{\bullet-}$ was used and far too much Np appeared to have been formed. Analysis of the results for **1a** and **1d** reported by Singh and Khanna shows that their 2:1 data have the same apparent misbalance as ours. However, the apparent excessive amount of Np measured in our GC analyses is understandable. It arose from the decomposition of the excess of $Np^{\bullet-}$ by water added in workup (eq 8),[14] which converted the $Np^{\bullet-}$ into

$$2Np^{\bullet-} + 2H_2O \rightarrow Np + DHNp + 2OH^- \quad (8)$$

equal amounts of Np and DHNp. The peaks for Np and 1,4-DHNp were coincident on our GC column. Overlap with the peak for 1,2-DHNp occurred, too, but was not complete. We assume that the same accounting can be applied to the data of Singh and Khanna. The results in Table 1 and the summation of material balances in Table 5, therefore, are consistent with eqs 6–8.

Reactions of 1f with $Np^{\bullet-}$. In broad principle, the reaction of **1f** is no different from that of the series **1a**–**d** (Scheme 2). Symmetrization (**3f**, Table 2) is the major pathway. Again, the yield of **3f** is greater in the 1:1 reaction (run 9) than in the 2:1 reactions (runs 10, 11). Small but significant amounts of **2f** and the cyclization product (**7**) were also obtained. In these respects our results differ from that of reaction of **1f** with nitropropanate ion in which **3f** (17%) was the only product. Our quantitative results are summarized in Table 5, showing good material balances. An unexpected product, phenol (**8**), is also listed in Table 2. The source of phenol was the reaction of **2f** itself with $Np^{\bullet-}$. This was shown independently (Experimental Section), and it was found also with GC and GC/MS that three other products, having the same mass as **2f**, were formed from the reaction of **2f** with $Np^{\bullet-}$. These products were also detected with GC in the reactions of **1f** with $Np^{\bullet-}$. No attempt was made to isolate and identify these products, however. In contrast, **7** was found not to react with $Np^{\bullet-}$. The amounts of **8** that are listed in Table 2 include the small amounts of these products, to which a GC response factor (R_f) was arbitrarily assigned as equal to the average of those of **2f** and **7**. It is evident from the results in Table 2 that the radical **4** must have been formed in order to lead to **7**. However, it is also evident that this is a minor pathway in comparison to symmetrization. It seems unlikely that **4** is responsible for symmetrization. Rather, symmetrization appears to occur before the breaking of an aryl–Hg bond. In our view, the more likely intermediates in that case are ArHgCl or $ArHg^{\bullet}$, that is, in which mercury is in the more common +2 or +1 oxidation states. The first of these possibilities corresponds with Russell's proposal for the reduction of $HgCl_2$ in a preexisting equilibrium (eq 1). The second calls for the formation of and extrusion of Hg from ArHgHgAr (eq 5). The way of formation of ArHgHgAr is either by the dimerization of $ArHg^{\bullet}$ or by the reductive decomposition of a complex of $ArHg^{\bullet}$ with ArHgCl (eq 9).

Scheme 2



$$ArHg^{\bullet} + ArHgCl \xrightarrow{e^-} ArHgHgAr + Cl^- \quad (9)$$

It is possible, also, to call on Todhunter and Currell's use of $ArHg^-$ in the symmetrization reaction (eqs 3 and 4). The drawback to that is its placing of mercury in the zero oxidation state. Yet, as will be seen with our reactions of Ar_2Hg, this may be unavoidable. The work of Todhunter and Currell demonstrates, incidentally, that reaction of Ar^- with ArHgCl cannot be the route to Ar_2Hg, since their reaction was carried out in ethanol in which Ar^- would not have survived.

Table 2 lists the ratios (**2f** + **8**)/**7** and **2f**/**8**. The first of these ratios shows that the lesser fate of radical **4** is

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(13) Streitwieser, A., Jr.; Scannon, P. J.; Niemeyer, H. M. *J. Am. Chem. Soc.* **1971**, *94*, 7936.

(14) Bank, S.; Closson, W. D. *Tetrahedron Lett.* **1965**, 1349.

(15) Sipos, J. C.; Sawatzky, H.; Wright, G. F. *J. Am. Chem. Soc.* **1955**, *77*, 2759.

Scheme 3

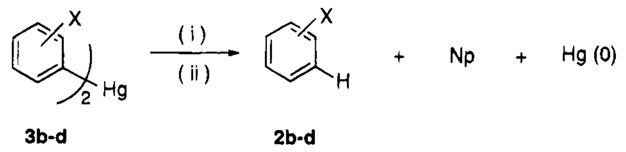
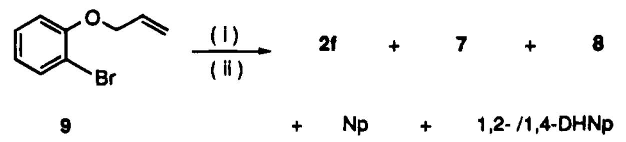


Table 3. Products of Reaction of Diarylmercurials (3b–d) with Sodium Naphthalenide (Np$^{\bullet-}$)[a]

		mmol × 10^2		products, mmol × 10^2 and %[b]		
run		3	Np$^{\bullet-}$	2	Np[c]	Hg
12	**3b**	35	69	65	67	32
				93	97	91
13	**3c**	23	46	42	44	21
				98	96	91
14	**3d**	23	46	43	44	21
				93	96	91

[a] In THF at room temperature. Solution of **3** added to solution of Np$^{\bullet-}$. [b] Second entry in each run. [c] Including small amounts of 1,2- and 1,4-DHNp.

Scheme 4



cyclization (leading to **7**) and that, as noted by others, reduction of **4** to anion **6** (the source of **2f**) is competitively rapid. The second ratio shows the susceptibility of **2f** to cleavage (leading to phenol) and isomerization by Np$^{\bullet-}$, those reactions being more pronounced in an environment of excessive Np$^{\bullet-}$.

Reactions of Diarylmercurials (3) with Np$^{\bullet-}$. Reactions of **3b–d** gave high yields of arene (**2b–d**) and Hg (Scheme 3). We chose not to use **3a** because of the more difficult assay of benzene that was required. The results are listed in Table 3. Reaction of Np$^{\bullet-}$ with **3f** was also carried out but, for convenience, the results are not included in Table 3 but are given in the Experimental Section. The products were **2f** (47%), phenol (29%), and (assumed) phenyl 1-propenyl ether (15%). None of **7** was obtained. The collective results call for reduction of **3** without the detectable formation of an aryl radical intermediate (eq 10). If reduction occurs in stages, i.e.,

$$\mathrm{Ar_2Hg + 2Np^{\bullet-} \xrightarrow{SH} 2ArH + Hg + 2Np} \qquad (10)$$

$$\mathrm{Ar_2Hg + Np^{\bullet-} \rightarrow Ar^- + ArHg^{\bullet} + Np} \qquad (11)$$

$$\mathrm{ArHg^{\bullet} + Np^{\bullet-} \rightarrow ArHg^- + Np} \qquad (12)$$

$$\mathrm{ArHg^- \rightarrow Ar^- + Hg} \qquad (13)$$

$$\mathrm{Ar^- \xrightarrow{SH} ArH} \qquad (14)$$

eqs 11–14, the formation and decomposition of ArHg$^-$ must be invoked. Our reaction with **3f** differs from that with **1f** in that **7** was not formed from **3f**.

Reaction of 9 with Np$^{\bullet-}$. The products of reaction (Scheme 4) are similar to those of reaction of **1f**, except, of course, for symmetrization. Run 15 (Table 4) shows that when equimolar amounts of reactant were used, half of the **9** was recovered, attesting to the stoichiometric ratio Np$^{\bullet-}$/**9** of 2:1. The formation of **7** shows that radical **4** was formed and that it cyclized to **5**. The distribution of products in the two runs, 15 and 16, is again instructive. There is not much difference in the yield of **7**, but there are significant differences in the yields of arene (**2f**) and phenol (**8**). It is apparent that addition of **9** to Np$^{\bullet-}$ (run 16) caused a decrease in the yield of **2f** and increase in that of **8**. Since the formation of **8** is attributable to reaction of **2f** with Np$^{\bullet-}$, the sense of the competing reaction, arene formation and cyclization, is again obtained from the ratio (**2f** + **8**)/**7**. Reaction of **2f** with Np$^{\bullet-}$, as noted earlier, gave not only **8** but some amounts of three other products, so that the amounts of those products are properly included in the comparison with the amount of **7**. This has been done in Table 4, and it can be seen that the ratio, given as (**2f** + **8**)/**7**, is not largely different in the two runs. The large difference in the runs is in the ratio **2f**/**8** (in which the amount of **2f** again includes the unidentified products). That ratio is 10 times larger in run 15 than in run 16, resulting from the high concentration of Np$^{\bullet-}$ met by **9** (and thus **2f**) in the inverse addition of reactants, i.e., **9** added to Np$^{\bullet-}$. The data are more quantitative than those reported earlier for the corresponding iodo compound[5] and show again that although **4** has to be formed, reduction to **6** (leading to **2f** after protonation) is a very fast reaction, competitive with cyclization.

Table 4. Products of Reaction of Allyl 2-Bromophenyl Ether (9) with Sodium Naphthalenide (Np$^{\bullet-}$)[a]

	mmol × 10^2		products, mmol × 10^2 and %[b]					ratio[c]	
run	**9**	Np$^{\bullet-}$	**2f**	**7**	**8**[c]	Np[d]	**9**[e]	(**2f** + **8**)/**7**	**2f**/**8**
15[f]	33	34	11	3.6	0.59	31	17	3.2	19
			69[g]	23[g]	3.7[g]	91	52		
16[h]	20	42	8.5	5.5	3.9	39		2.4	1.8
			43	28	20	93			

[a] In THF at room temperature. [b] Second entry in each run. Yields from **9** are based on Ar group content. [c] Included in the amount of **8** in run 16 are the amounts of three other products (0.89 × 10^{-2} mmol), *m/e* 134, believed to have been formed from **2f** in its reaction with Np$^{\bullet-}$. [d] Sum of Np, 1,2- and 1,4-DHNp. [e] Recovered. [f] Np$^{\bullet-}$ added to **9**. [g] After compensating for recovered **9**. [h] **9** added to Np$^{\bullet-}$.

Table 5. Material Balances (%) in Products from Reactions of 1, 3, and 9 with Sodium Naphthalenide

	balance in products		
run[a]	Ar	Hg	Np
1[b]	94	92	93
2	94	94	91
3[b]	92	92	92
4	103	88	95
5[b]	97	95	92
6	100	92	95
7[b]	99	91	93
8	100	91	90
9[b]	95	96	94
10	99	90	92
11	98	90	94
12	93	91	97
13	98	91	96
14	93	91	96
15	95		91
16	94		93

[a] See Tables 1–4. [b] After compensating for unused reactant.

We conclude that one-electron transfer to arylmercuric chlorides leads initially to symmetrization (Ar$_2$Hg) by a route in which free aryl radicals are not involved and without breaking of an Ar–Hg bond. Further reduction of Ar$_2$Hg leads to arene ArH, again without involvement of free aryl radical.

Experimental Section

Tetrahydrofuran (THF, Fisher T397-4) was dried by distillation from $LiAlH_4$ and was stored under argon. Allyl phenyl ether (**2f**) and phenylmercuric chloride (**1a**) from Aldrich, 1,2-dihydronaphthalene (DHNp) from Lancaster, 1,4-dihydronaphthalene from Wiley Organics, diphenylmercury (**3a**) from Alpha-Ventron, and di-*p*-tolylmercury (**3d**) from Eastman Kodak were used as received. 3-Methyl-2,3-dihydrobenzofuran (**7**) was prepared as described earlier.[9] Di-*p*-anisylmercury (**3c**) had been prepared in these laboratories earlier[9] and was recrystallized from absolute ethanol, mp 230−231 °C. Arylmercuric chlorides **1b−d** were prepared by reaction of the corresponding Ar_2Hg with $HgCl_2$ in absolute ethanol. **1b**, crystallized from benzene, had mp 180−181 °C (lit.[15] mp 179 °C); **1c**, crystallized from acetone, had mp 250−252 °C (lit.[16] mp 249−250 °C); **1d**, crystallized from chloroform, had mp 237−239 °C (lit.[17] mp 238−239 °C). **1f** was prepared as described by Russell[1] and had mp 93−95 °C (crystallized from ethanol). **1e** was prepared from the double salt of *p*-nitrobenzenediazonium chloride and $HgCl_2$ as described[18] and had mp 264−266 °C (crystallized from ethanol) (lit.[18] mp 265 °C).

Di-*o*-anisylmercury (**3b**) was prepared by reaction of 2-bromoanisole with NaHg, mp 107−108 °C (crystallized from methanol) (lit.[19] mp 108 °C).

Di[*o*-(allyloxy)phenyl]mercury (**3f**) was prepared from allyl 2-bromophenyl ether[20] as described by Russell,[1] mp 69−70 °C (lit.[1] mp 69−70.5 °C).

Quantitative gas chromatographic analyses were made on a 1/8-in., 4-ft stainless steel column of 10% OV-101 on 80−100 mesh Chrom WHP in a Varian 3700 FID chromatograph attached to a Spectra Physics 4290 integrator. The injector and detector temperatures were 250 and 300 °C, respectively, and the oven temperature was held at 50 °C for 2 min and ramped at 10 °C/min to 250 °C. Authentic compounds and their predetermined response factors were used, with dibutyl ether as an internal standard. 1,2-DHNp was not completely separable from naphthalene, and 1,4-DHNp was coincident with naphthalene on our GC column. Therefore, our assays of Np include 1,2- and 1,4-DHNp. Mass spectra, used in monitoring GC analyses, were obtained with a Hewlett-Packard Model 5995 spectrometer.

Reactions of ArHgCl with Sodium Naphthalenide. Two modes of addition of reactants were used. In one mode, the ArHgCl was placed under argon in a septum-capped, 10-mL volumetric flask containing a stirrer bar, and 5 mL of THF was added by syringe. A solution of $Na^+Np^{\bullet-}$ in 5 mL of THF was next added by syringe while the mixture was stirred rapidly. The dark green color of $Np^{\bullet-}$ was discharged within a few minutes. After 1 h of stirring a few drops of water were added. The gray precipitate of Hg was separated by centrifugation, and the supernatant solution was removed with a pipette for GC analysis. The Hg was washed with water and acetone under centrifugation, allowed to dry, and weighed in the tube. In the second mode, 5 mL of $Na^+Np^{\bullet-}$ solution was placed in the volumetric flask, under the same conditions, and the solution of ArHgCl was added dropwise by syringe. The same procedure was followed. The mode of addition, quantities of reactants, and results of analyses are given in Tables 1 and 2.

Reactions of Diarylmercurials with $Na^+Np^{\bullet-}$. Reactions were carried out with **3b−d,f**, in principle as described for reactions of ArHgCl. With **3b−d**, a solution of **3** was added to a solution of $Na^+Np^{\bullet-}$, and the results are listed in Table 3. When this mode of addition was used with **3f**, a poor GC material balance was achieved. Dropwise addition of the $Na^+Np^{\bullet-}$ solution (0.35×10^{-2} mmol) to the solution of **3f** (0.17×10^{-2} mmol) gave (in mmol $\times 10^2$) **2f** (0.16, 47%), **8** (0.10, 29%), Np (0.32, 91%), and Hg (0.16, 94%). None of **7** was found. Apart from **2f**, another product with similar GC and GC/MS characteristics was obtained, which we assume may have been phenyl 1-propenyl ether. With an assumed R_f equal to that of **2f**, the amount was 0.051×10^{-2} mmol, 15%.

Reaction of 2f and 7 with $Na^+Np^{\bullet-}$. A solution of 0.45×10^{-2} mmol of **2f** in 5 mL of THF was added to a solution of 0.91×10^{-2} mmol of $Na^+Np^{\bullet-}$ in 5 mL of THF. Workup and GC analysis gave 0.094×10^{-2} mmol (21%) of **8**, 0.86×10^{-2} mmol (95%) of Np (and DHNp), and three other compounds with mass 134. These were not identified. By assigning to them an R_f equal to the average of the R_f for **2f** and **7**, the sum of these compounds was 0.29×10^{-2} mmol (64%). In contrast, when **7** was used similarly and the mixture of reactants was stirred for 28 h, all of the **7** was recovered.

Reactions of Allyl 2-Bromophenyl Ether with $Na^+Np^{\bullet-}$. The same procedures were used as with reactions of ArHgCl. Results are given in Table 4.

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(16) Torssell, K. *Acta Chem. Scand.* **1959**, *13*, 115.

(17) Nesmejanow, A. N. *Chem. Ber.* **1929**, *62*, 1010.

(18) Nesmejanow, A. N.; Glushnew, N. Th.; Epifansky, P. Th.; Flegontow, A. I. *Chem. Ber.* **1934**, *67*, 130.

(19) Michaelis, A. *Chem. Ber.* **1894**, *27*, 244.

(20) Hurd, C. D.; Webb, C. N. *J. Am. Chem. Soc.* **1936**, *58*, 941.