

SODIUM NAPHTHALENE INDUCED REDUCTIVE DEMERCURATION AND
SYMMETRIZATION OF ORGANOMERCURIC HALIDES

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Summary: A novel electron transfer free radical mechanism has been elucidated for the sodium naphthalene induced demercuration and symmetrization of some alkyl- and arylmercuric chlorides.

Naphthalene radical anion is known to reduce arenediazonium cations¹ and certain benzylic halides² via $\pi^* - \pi^*$ electron transfer pathways. Reduction of organomercuric halides has been effected by a variety of reductants such as sodium metal,³ sodium stannite,⁴ and hydrazine;⁵ but the mechanistic details are obscure. Continuing our research interest in the electron transfer reaction mechanisms,⁶⁻⁸ we have examined the reactions of certain organomercuric chlorides 1 with naphthalene radical anion and present here the first report on the occurrence of an electron transfer free radical mechanism in these reactions.

The reactions of benzylmercuric chloride, $C_6H_5CH_2-Hg-Cl$ 1a, and arylmercuric chlorides, $p-R-C_6H_4-Hg-Cl$ (1b, 1c, 1d where $R = H, CH_3, NO_2$, respectively) with varying amounts of sodium naphthalene in THF solvent, at 30°C, under nitrogen atmosphere gave the results summarized in the Table. The reactions with equimolar amounts of sodium naphthalene in 30 min (runs 1, 8, 13 and 15) were largely incomplete; but on increasing the reaction time, more of the organomercuric chloride 1 reacted in each case. The reactions of 1a, 1b and 1d were complete in 30 min with twice the molar quantities of sodium naphthalene, but only 88% of 1c reacted under similar conditions. The conceivable formation of alkyl/aryl anions in runs 7 and 12 (reactions with equimolar quantities of sodium naphthalene) is ruled out in view of our inability to trap⁹ these species in separate control experiments. It is evident from run 6 that in the presence of cumene, reductive demercuration predominates over symmetrization. All these facts become discernible if intervention of radicals is visualized in these reactions. The formation of radicals via nucleophilic displacement of Cl^- by naphthalene radical anion on the electrophilic mercury of 1, followed by homolytic cleavage of the C-Hg bond into RHg^\bullet radicals and naphthalene, is unlikely since 9-fluorenyl anion, an¹⁰ equally good nucleophile, does not react with 1b by an S_N2 displacement process.

In view of the known electron donating ability^{1,2} of naphthalene radical

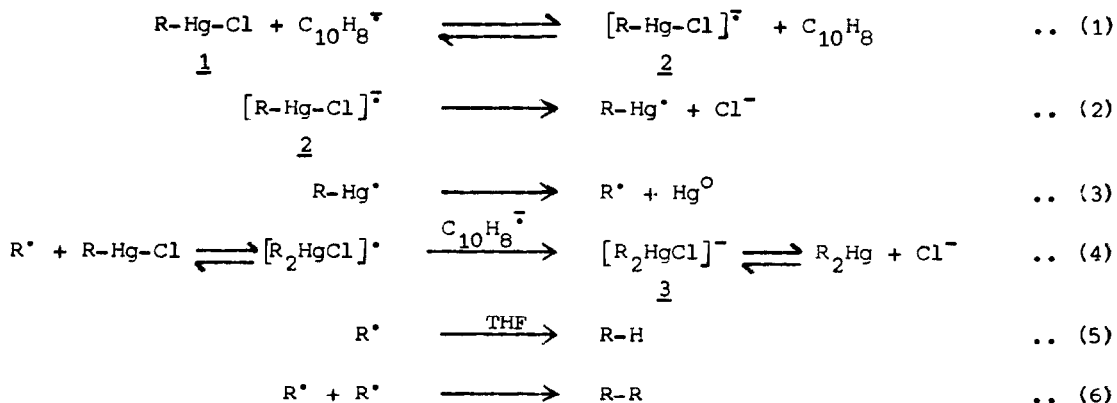
Table: Reactions^a of organomercuric halides 1 with sodium naphthalene

Run	Organo- mercuric halides R-Hg-Cl, <u>1</u>	Molar ratio $C_{10}H_8^{\bar{2}}:1$	Reac- tion time (min)	% yield of products ^b				
				R-Hg-R	R-H	R-R	Naphth- alene ^c	Starting halide <u>1</u>
1	<u>1a</u>	1.00	30	21	2	9	85	69
2	<u>1a</u>	1.00	360	24	3	12	89	62
3	<u>1a</u>	2.00	30	46	30	16	90	-
4 ^d	<u>1a</u>	1.00	30	13	2	5	92	78
5 ^d	<u>1a</u>	2.00	30	41	26	13	90	12
6 ^e	<u>1a</u>	2.00	30	6	46	3	87	31
7 ^f	<u>1a</u>	1.00	30	20	2	8	89	67
8	<u>1b</u>	1.00	30	32	12	3	88	51
9	<u>1b</u>	1.00	360	36	14	3	93	45
10	<u>1b</u>	2.00	30	53	38	2	92	-
11 ^d	<u>1b</u>	1.00	30	24	8	2	90	60
12 ^f	<u>1b</u>	1.00	30	31	10	3	90	53
13	<u>1c</u>	1.00	30	23	6	2	85	70
14	<u>1c</u>	2.00	30	45	36	2	91	12
15 ^g	<u>1d</u>	1.00	30	33	3	2	90	35
16 ^g	<u>1d</u>	2.00	30	31	29	2	84	-

- a. 5×10^{-3} mol of R-Hg-Cl were reacted with $Na^+ C_{10}H_8^{\bar{2}}$ in THF, at 30°C, under nitrogen atmosphere.
- b. Percentage based on organomercuric halides, unless otherwise stated. An unestimated amount of metallic mercury was also obtained in these reactions. Mercury was separated from other products during work up by filtration through celite.
- c. Percentage based on sodium naphthalene.
- d. In the presence of 5×10^{-3} mol naphthalene added from outside. Yield of naphthalene based on the total amount of naphthalene, obtainable from initially used $Na^+ C_{10}H_8^{\bar{2}}$ as well as $C_{10}H_8$ added from outside.
- e. In the presence of cumene (0.1 mol).
- f. In the presence of $MgBr_2$ (0.01 mol). On subsequent reaction with benzophenone, not even a trace of benzylidiphenylcarbinol in run 7 and triphenylcarbinol in run 12, was detected.
- g. Unestimated amounts of azobenzene and azoxybenzene were also obtained. Additional mixture of coloured products could not be analyzed.

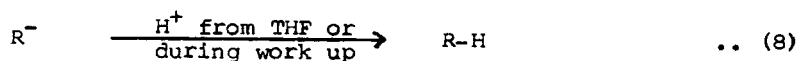
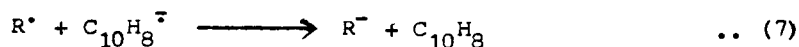
anion towards appropriate substrates and the fact that organomercuric halides accept electrons even from relatively weaker reducing agents,¹¹ we propose the occurrence of an electron transfer free radical mechanism outlined in the scheme to rationalize all the observations recorded for the title reactions.

SCHEME



The reaction is initiated by the transfer of an electron from the π^* MO of naphthalene radical anion to the lowest unoccupied molecular orbital (LUMO) of 1. The reversibility of step 1 is evident from the retardation of the reactions of 1a and 1b in the presence of added naphthalene¹² (runs 4, 5 and 11). The radical anion 2 formed in step 1 fragments¹³ to yield the highly unstable R-Hg $^{\cdot}$ radical and Cl $^-$ ion. The decomposition of the radical R-Hg $^{\cdot}$ to yield the radical R $^{\cdot}$ and metallic mercury is known¹⁴ to be rapid at our reaction temperature. The R $^{\cdot}$ radical may then add to 1 giving an adduct^{14, 15a} which on acceptance of an electron from naphthalene radical anion would yield the symmetrical diorganomercurial R-Hg-R (step 4), dimerize to form R-R (step 6) or abstract a hydrogen atom from the solvent to produce the hydrocarbon R-H (step 5). Anion 3 may undergo reversible cleavage of the Hg-Cl bond as shown in step 4; but does not fragment into 1 and R $^-$ anion.^{15b} As cumene donates a hydrogen atom to R $^{\cdot}$ radical with ease, the observed increase in the yield of toluene at the expense of dibenzylmercury and bibenzyl in run 6, establishes the formation of these products via the benzyl radical C₆H₅CH₂ $^{\cdot}$. The C-H bond strength being greater than the Hg-H bond strength,¹⁶ the hydrogen atom abstraction by R-Hg $^{\cdot}$ radical from cumene to yield R-Hg-H, is unlikely.

Alkyl or aryl anions may be formed from the corresponding radicals in the presence of an excess of naphthalene radical anion, (Eq. 7).² This is in agree-



ment with the observed increase in the yields of monomeric hydrocarbons R-H, in the reactions of organomercuric chlorides carried out with twice the molar quantities of sodium naphthalene (runs 3, 10, 14 and 16).

The diorganomercurials formed in these reactions may also be reduced, though more slowly, by a similar electron transfer from naphthalene radical anion. Indeed, our initial experiments on the reaction of dibenzylmercury with sodium naphthalene have indicated the formation of toluene, bibenzyl and metallic mercury.

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References and Notes

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10. The reaction of equimolar amounts of 1b and 9-fluorenyl lithium in THF at 30°C under N₂ atmosphere for 30 min was incomplete and 83% of 1b was recovered back. Though phenyl fluorenyl mercury is stable under our reaction conditions, it is obtained only in traces in this reaction. In addition, diphenylmercury 9%, 9-phenylfluorene 4%, fluorene 81%, difluorenyl 10%, a trace of bifluorenylidene and an unestimated amount of metallic mercury were also obtained.
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