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Cation Radicals. 48. Evidence for Electron Transfer in the Alkylation of Thianthrene Cation Radical with Diethylmercury[1,2]

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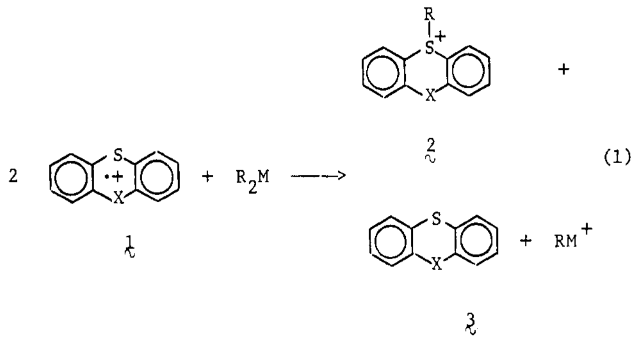
Evidence is presented that reaction of thianthrene cation radical ($Th^{+}\cdot$) with Et_2Hg in acetonitrile occurs by way of initial electron transfer. Products of reaction are thianthrene (Th), 5-ethylthianthrenium perchlorate ($ThEt^{+}ClO_4^{-}$), and $EtHg^{+}$. When reaction is carried out under $^{18}O_2$, not only the same products are formed but also thianthrene oxide (ThO), thianthrene dioxide (ThO_2), acetaldehyde, and ethanol, all of which are enriched with ^{18}O. Reaction therefore appears to lead initially to $Et_2Hg^{+}\cdot$ from which ethyl radicals are formed and are trapped with $Th^{+}\cdot$ and O_2. Reactions of $EtO_2\cdot$ are believed to lead to the products containing ^{18}O. Reaction of Ph_2Hg with $Th^{+}\cdot$ does not appear to follow this pathway.

In 1978 thianthrene and phenoxathiin cation radicals (**1a,b**) were shown to react with dimethyl-, diethyl-, and a number of diarylmercurials according to eq 1.[4] The stoichiometry of eq1 is that which is commonly seen in reactions of cation radicals,[5] that is, in which half of the amount of cation radical is converted into product and half into the parent compound. In the organometal reactions excellent yields of products were obtained, corresponding with the stoichiometry shown, except when diethylmercury (Et_2Hg) was used. In that case the yield of **2a** (R = Et) was 39%, while the yield of thianthrene (**3a**) was 131%.



R = aryl, Me, Et; M = Hg, Zn.

1a, 2a, 3a, X = S; 1b, 2b, 3b, X = O

The mechanism of these novel S-alkylation and arylation reactions was not known. It was pointed out that the reactions with diarylmercurials resembled the protonolyses of diarylmercurials.[6] That is, the reactions were inhibited by the presence of an electron-withdrawing group in the ring and appeared, from the position of substitution, to be direct displacements of mercury from the ring by the sulfur atom of the cation radical. Furthermore, the relatively slow reactions of the diarylmercurials, as compared with the two dialkylmercurials, and the effect of ring substituents appeared to be qualitatively analogous to the rate-limiting protonolyses of diarylmercurials.[7] In contrast with reactions of diarylmercurials, those of the dialkylmercurials were thought to resemble the electron-transfer reactions of dialkylmercurials which had been reported by Kochi and co-workers with carbon tetrachloride[8] and hexachloroiridium(IV) ion[9] and by Russian workers with quinones.[10,11]

In those reactions, electron transfer led to the dialkylmercurial cation radical ($R_2Hg^{+}\cdot$) which decomposed rap-

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[1] Part 47: Stephenson, M. T.; Shine, H. J. *J. Org. Chem.* **1981**, *46*, 3139.

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[3] On leave from Kinki University, Hiroshima, Japan.

[4] Bandlish, B. K.; Porter, W. C., Jr.; Shine, H. J. *J. Phys. Chem.* **1978**, *82*, 1168.

[5] Bard, A. L.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155.

(6) (a) Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968; pp 64, 178. (b) Abraham, M. H. In "Comprehensive Chemical Kinetics"; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: New York, 1972; Vol. 12, pp 49, 112. (c) Matteson, D. S. "Organometallic Reaction Mechanisms"; Academic Press: New York, 1974.

[7] Nugent, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5979.

[8] Nugent, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5405.

[9] Chen, J. Y.; Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 6150.

[10] Abakumov, G. A.; Gladyshev, E. N.; Vyazankin, N. S.; Razuvaev, G. A.; Bayushkin, P. Ya.; Muraev, V. A. *J. Organomet. Chem.* **1974**, *64*, 327.

[11] Abakumov, G. A.; Muraev, V. A.; Razuvaev, G. A.; Tikhonov, V. D.; Chechet, Y. V.; Nechnev, A. K. *Dokl. Chem.* (*Engl. Transl.*) **1976**, *230*, 571.

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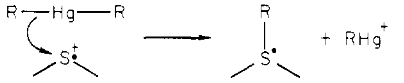
idly into RHg^+ and the alkyl radical, R·. Kochi found that when reactions of R_2Hg with $Ir^{IV}Cl_6^{-2}$ were carried out under oxygen, the R· radicals were diverted from their normal reaction pathway by rapid reaction with oxygen, and the products of that reaction appeared as alcohols, aldehydes, and ketones. Because all of our cation radical reactions had been carried out in air but nevertheless, except for Et_2Hg, gave excellent yields of products, we were somewhat skeptical of accepting the role of an electron-transfer step in the reactions. It was thought that among the reactions studied only that with Et_2Hg appeared to support an electron-transfer step because of the low yield of **2a** (R = Et) and the corresponding high yield of **3a**.

The contrast in the two mechanisms is illustrated with eq 2 and 3 for direct displacement and with eq 4–6 for



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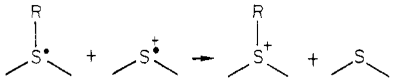

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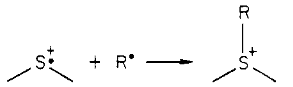
$$R_2Hg^{+\cdot} \rightarrow R\cdot + RHg^+ \quad (5)$$



(6)

electron transfer, in which the sulfur cation radical is abbreviated as $S^{+\cdot}$. The direct displacement mechanism is, in principle, like the so-called half-regeneration reactions frequently seen in cation radical reactions.[5]

We have now reinvestigated the reaction of Et_2Hg with **1a** (symbolized here as $Th^{+\cdot}$) in an atmosphere of oxygen and oxygen-free argon. We have sought and found evidence for the presence of ethyl radicals. For comparison we have carried out similar reactions with diphenylmercury (Ph_2Hg).

Results and Discussion

The reaction of Et_2Hg with $Th^{+\cdot}$ is very fast. The reaction was carried out by injecting the neat Et_2Hg from a syringe into a stirred solution of $Th^{+\cdot}ClO_4^-$ in acetonitrile; the color of $Th^{+\cdot}$ was discharged immediately. When the reaction was carried out under argon, the only products isolated were thianthrene (Th), the adduct **2a** (isolated as $ThEt^+ClO_4^-$), $EtHg^+$ (isolated, because of deliberate addition of LiCl in the workup, as EtHgCl), and some thianthrene 5-oxide (ThO). The source of the ThO is the well-known reaction of $Th^{+\cdot}$ with water remaining in the incompletely dried solvent (eq 7).[5] The yields of anticipated products were very good and are given in Table I.

$$2Th^{+\cdot} + H_2O \rightarrow Th + ThO + 2H^+ \quad (7)$$

Reaction under oxygen also gave the usual products. Conversion of $Th^{+\cdot}$ into $ThEt^+$ was not stopped by the presence of oxygen. At the same time three new products were found: acetaldehyde, ethanol, and a small amount of thianthrene *cis*-5,10-dioxide (ThO_2, identified by TLC, mass spectrometry, and isolation). The acetaldehyde and ethanol were identified and assayed by GLC. They were not found (by GLC) either in reactions under argon or when Et_2Hg alone was kept in acetonitrile under oxygen for several hours.[12]

Table I. Source and Yields of Products from Reaction of Diethylmercury with Thianthrene Cation Radical ($Th^{\cdot+}$)

	experiment[a] (gas cover)			
reactants/results	1 (Ar)	2 ($^{16}O_2$)	3 ($^{16}O_2$)	4 ($^{18}O_2$)
$(Th^{\cdot+})_0$, mmol[b]	2.736	3.102	2.830	2.259
$(Et_2Hg)_0$, mmol	1.606	2.078	1.511	1.368
ThO from H_2O, %	7.5	2.7	20.4	12.5
ThO from $EtO_2\cdot$, %	0	19.4	6.2	14.7
Th (total),[c] %	102.3	100	100	100
$ThEtClO_4$,[d] %	89.2	86.1	102	95.2
EtHgCl,[e] %	95.9	91.9	99.1	99.4
acct of $(Th^{\cdot+})_0$,[f] %	97.7	95.8	100.5	99.9

[a] In 30 mL of CH_3CN. [b] As $Th^{\cdot+}ClO_4^-$. [c] The Th isolated represents Th formed by electron transfer (eq 8) and the water reaction (eq 7) and lost by oxidation (eq 13). The amount of Th formed by electron transfer was assumed to be equivalent to the $(Et_2Hg)_0$, an assumption made reasonable by the high isolated yields of EtHgCl. [d] Based on the amount of $Th^{\cdot+}$ available for reaction with Et· (eq 10) after reactions 7 (with H_2O) and 8 (with Et_2Hg) had occurred. Reaction 7 was assumed to occur without hindrance during the lengthy purging and degassings of the solution of $Th^{\cdot+}$ in acetonitrile. [e] Based on $EtHg^+$ from reactions 8 and 9 and $(Et_2Hg)_0$. [f] The amount of $(Th^{\cdot+})_0$ used up and equated to the products formed (and isolated) from the sequence of reactions 7, 8, and 10.

When reaction was carried out under labeled oxygen (ca. 20% $^{18}O_2$), ^{18}O was found by mass spectrometry to be incorporated in the products ThO, ThO_2, acetaldehyde, and ethanol. The ratio $100(m + 2)/m$ for ThO was 25.5 and for ThO_2 was 17.8, whereas the calculated ratios for ordinary ThO and ThO_2 are 10.13 and 10.33, respectively. It is evident, therefore, that reaction of $Th^{+\cdot}$ with Et_2Hg under oxygen generated an O-atom carrier even though the formation of $ThEt^+$ was not stopped.

Heterocyclic cation radicals like $Th^{+\cdot}$ appear themselves to be inert to oxygen. They have been used for years in many studies of reactions with nucleophiles, and there is no evidence in those studies for the formation of ThO other than by reaction with water in solvents and none whatsoever for the formation of ThO_2.[5,13] There is no doubt, therefore, that in the Et_2Hg reactions under oxygen the formation of ThO_2 must be wholly due to an oxygen transfer reaction involving Et_2Hg. The formation of ThO must also be attributed in part to such a reaction. The formation of CH_3CHO and CH_3CH_2OH is attributable to reactions of $EtO_2\cdot$ radicals.[9]

We can account quantitatively for all products by assuming that the first reaction to occur is a one-electron transfer from Et_2Hg to $Th^{+\cdot}$ (eq 8) and that it is complete.

$$Th^{+\cdot} + Et_2Hg \rightarrow Th + Et_2Hg^{+\cdot} \quad (8)$$

$$Et_2Hg^{+\cdot} \rightarrow Et\cdot + EtHg^+ \quad (9)$$

$$Th^{+\cdot} + Et\cdot \rightarrow ThEt^+ \quad (10)$$

$$Et\cdot + O_2 \rightarrow EtO_2\cdot \quad (11)$$

$$EtO_2\cdot \rightarrow\ \rightarrow CH_3CHO/CH_3CH_2OH \quad (12)$$

$$Th + EtO_2\cdot \rightarrow ThO + EtO\cdot \quad (13)$$

$$ThO + EtO_2\cdot \rightarrow ThO_2 + EtO\cdot \quad (14)$$

This is followed by product-forming reactions (eq 9–14). Rapid decomposition[9] of $EtHg^{+\cdot}$ leads to $EtHg^+$, which is

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(12) Kochi and co-workers[9] have reported also that a series of dialkylmercurials did not react with oxygen in the absence of $Ir^{IV}Cl_6^{2-}$.

(13) Ando, W.; Kabe, Y.; Kobayashi, S.; Takyu, C.; Yamagishi, A.; Inaba, H. *J. Am. Chem. Soc.* **1980**, *102*, 4526. These authors have shown that $Th^{+\cdot}$ reacts with superoxide ion but not with oxygen. The reaction with superoxide ion leads subsequently to equal amounts of Th and ThO.

Table II. Yields[a] of Products from Reaction of Diphenylmercury with Thianthrene Cation Radical

expt	gas	$(\mathrm{Th}^{\cdot+})_0$, mmol	$(\mathrm{Ph_2Hg})_0$, mmol	% yield ThO	Th	ThPhClO$_4$	PhHgCl
5	Ar	3.000	1.527	7.7	103	97.1	92.1
6	$^{16}O_2$	3.042	1.681	4.7	99.6	96.8	89.9

[a] Based on the stoichiometry of eq 1, after allowing for formation of ThO (and Th) by the water reaction (eq 7) only.

isolated quantitatively in the workup as EtHgCl, and ethyl radicals (Et·). The ethyl radicals are scavenged by both $Th^{+}\cdot$ (eq 10) and O_2 (eq 11). If our presentation is correct, this means that $Th^{+}\cdot$ is a very effective scavenger of alkyl radicals. Other information regarding this possibility is, as far as we know, unavailable. We believe that the source of ThO, in part, and of ThO_2, wholly, is a reaction with $EtO_2\cdot$ (eq 13 and 14). We have not yet been able to generate $EtO_2\cdot$ radicals by other means in the presence of $Th^{+}\cdot$, but we have found that *t*-BuOOH slowly oxidized Th itself to ThO and ThO_2.

By assuming that electron exchange (eq 8) is rapid and complete and is followed by reactions as in eq 9–14, we are able to account for all of the $Th^{+}\cdot$ and Et_2Hg used in our reactions and for the amounts of products isolated. The formation of ThO occurs in two ways (eq 7 and 13), so that we have had to partition the yield of ThO between these two sources. This was accomplished with eq 15 and 16.

$$\text{Th (isolated)} = \text{Th(et)} + \text{Th(H}_2\text{O)} - \text{Th(EtO}_2\cdot) \qquad (15)$$

$$\text{ThO (isolated)} = \text{ThO(H}_2\text{O)} + \text{ThO(EtO}_2\cdot) \qquad (16)$$

In these equations the information in parentheses is the source of the product. That is Th(et) is from electron transfer and is assumed to be equal to the initial amount of Et_2Hg (eq 8). $Th(H_2O)$ and $ThO(H_2O)$ are from the water reaction (eq 7) and must be stoichiometrically the same, while $Th(EtO_2\cdot)$ and $ThO(EtO_2\cdot)$ are from the oxygen-atom-transfer reaction (eq 13) and are also stoichiometrically the same. Our calculations and assumptions require that the extent of the water reaction, which is relatively slow, varied from one experiment to another. But we feel that this is not unreasonable since the drying and handling of the solvent acetonitrile occurred at different times, and the duration of purging procedures also varied. Last, we counted the small amounts of ThO_2 as ThO in our calculations, and again this is not in error if our presentation (eq 13 and 14) is correct.

Our results are given in Table I and have been set out to account for the amounts of $Th^{+}\cdot ClO_4^-$ and Et_2Hg used. Our results show that it was not possible to prevent the formation of the adduct $ThEt^+$ by carrying out the reaction under oxygen. The greater part of the $Th^{+}\cdot$ remaining after electron transfer (eq 8) and reaction with water (eq 7) did, in fact, react with ethyl radicals (eq 10). At the same time, however, the formation of acetaldehyde and ethanol leave no doubt that ethyl radicals were scavenged by oxygen. Assays of these products by GLC corresponded with 11.5% and 36%, respectively, of the ethyl radicals that could be formed (eq 9). The formation of acetaldehyde and ethanol by the trapping of ethyl radicals with oxygen was confirmed with the use of $^{18}O_2$, when these products were shown by mass spectrometry to be enriched in ^{18}O. Enrichment of ^{18}O was also found in the ThO and ThO_2.

In contrast with reaction of Et_2Hg with $Th^{+}\cdot$, the reaction of Ph_2Hg was very slow, continuing over periods of days. We could find no certain evidence (e.g., biphenyl) for phenyl radicals having been formed, except, possibly, that under both argon and oxygen very small amounts of benzene were detected by GLC. Phenol could not be found in the reaction under oxygen. The reaction of phenyl radicals with oxygen is very fast,[14] and we have assumed that if phenyl radicals are formed in the Ph_2Hg reaction some should be trapped with oxygen. In that case the PhOO· radicals might also then decompose into biphenyl[15] or phenol. Noticeably also, the amount of ThO formed in the reaction with Ph_2Hg under oxygen was smaller, in fact, than in the reaction under argon (Table II), which also suggests that the reaction of Ph_2Hg with $Th^{+}\cdot$ is unlike that of Et_2Hg. The yields of products from the Ph_2Hg reactions, after compensation for the water reaction (eq 7) were very good. It appears that if electron exchange does occur in the reaction of Ph_2Hg with $Th^{+}\cdot$, it has not been detected in our experiments. Thus, the reaction appears to correspond with what we have called direct displacement, but this may, in fact, be the product-forming collapse of a charge-transfer complex[16] without the formation of free phenyl radicals.

A measure of the relative ease of electron transfer from Ph_2Hg and Et_2Hg to $Th^{+}\cdot$ could be obtained from the oxidation potentials of Ph_2Hg and Et_2Hg, but these are not known exactly. The cyclic voltammograms of Ph_2Hg and Et_2Hg are completely irreversible,[17,18] but we have measured the peak potentials of their anodic waves in cyclic voltammetry and they are 1.48 V for Et_2Hg and approximately 2.20 V for Ph_2Hg (vs. SCE, 0.10 M tetrabutylammonium perchlorate in acetonitrile),[19] indicating that electron transfer from Ph_2Hg should be the more difficult.[20]

As far as we are aware no other reactions of $Th^{+}\cdot$ or other organosulfur cation radicals have been reported in which *product formation* is preceded by one-electron transfer. The possibility that such product-forming transfer reactions can occur, e.g., with nitrite and halide ions, has been discussed, however.[5] Certainly, electron transfer from nucleophiles to organosulfur cation radicals is known to occur, e.g., with cyanide ion, but such reactions do not give adducts, either at sulfur or ring positions. It may well be that adducts *could* be formed by, say, the slow mixing of

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[14] Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589.

[15] Russell, G. A.; Bridger, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 3765.

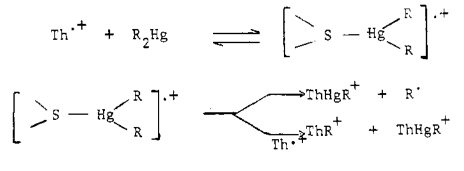
[16] Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928.

[17] Fleischman, M.; Pletcher, D.; Sundholm, G. *J. Electroanal. Chem.* **1971**, *31*, 51. These authors report $E_{p/2}$ for Ph_2Hg as 1.84 V vs. Ag/Ag^+ (0.1 M), from which we can estimate a value for 2.14 V vs. SCE.

[18] Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790. These authors have reported the irreversibility of the cyclic voltammograms of a number of dialkylmercurials.

[19] We thank Dr. W. H. Smith for these measurements.

[20] A referee has suggested that another mechanism may account for our results. This is shown in the equations below in which also the free



RHg+, which we propose, becomes complexed with Th. In this mechanism it is intended that the formation of ThR^+ does not occur by scavenging of R· by $Th^{+}\cdot$. In turn this is designed to account for the fact that the yield of ThR^+ is not much influenced by carrying out the reaction under the scavenger oxygen.

Table III. Quantities of Reactants and Isolated Products from Reaction of Th$^{\cdot+}$ClO$_4^-$ with R$_2$Hg[a]

		mmol					
expt	R	Th$^{\cdot+}$	R$_2$Hg	Th	ThO	ThRClO$_4$	RHgCl
1	Et[b]	2.74	1.61	1.75	0.102	0.826	1.54
2	Et[c]	3.10	2.08	1.52	0.643	0.809	1.91
3	Et[c]	2.83	1.51	1.62	0.465	0.757	1.50
4	Et[c]	2.26	1.37	1.18	0.473	0.579	1.36
5	Ph[b]	3.00	1.53	1.55	0.116	1.35	1.28
6	Ph[c]	3.04	1.68	1.52	0.071	1.40	1.30

[a] In 30 mL of acetonitrile. [b] Under argon. [c] Under oxygen.

nucleophile and cation radical solutions. In that way a radical (e.g., CN·) formed by electron transfer might react with remaining cation radical. Along these lines, Smith has reported that the slow, but not fast, addition of CN$^-$ solution to a solution of zinc octaethylporphyrin cation radical led to ring cyanation.[21]

Experimental Section

Diphenylmercury (Eastman) had a melting point of 124–125 °C and was used as obtained. Diethylmercury (Pfaltz and Bauer) was redistilled before use and had the following: bp 100–101 °C (115 mmHg); $n^{23}{}_{\mathrm{D}}$ 1.5414 (lit. $n^{22}{}_{\mathrm{D}}$ 1.5400).[22] Acetonitrile (Eastman) was distilled from phosphorus pentoxide, kept over molecular sieves, and distilled again from phosphorous pentoxide before use. Th^{+}·ClO$_4^-$ (extreme caution) was prepared as before.[23] Labeled oxygen (ca. 20% ^{18}O$_2$) was from BOC-Prochem.

Reaction Procedure. A weighed amount of freshly prepared Th^{+}·ClO$_4^-$ was placed in a three-necked flask containing a magnetic stirrer. The flask was equipped with a condenser, connecting tubing for the argon or ^{16}O$_2$ supply, and a rubber septum. After the flask was purged with the appropriate gas, 30 mL of acetonitrile was introduced by syringe through the septum. Argon flowed through two bottles of pyrogallol solution, two bottles of concentrated sulfuric acid, and a tube of soda lime. Ordinary oxygen was treated similarly except for the pyrogallol bottles. Labeled oxygen was introduced from a glass bulb, equipped with a break seal, after the acetonitrile solution had been degassed by the freeze–thaw technique twice. Each reaction mixture was kept under the appropriate gas by a slow gas flow (argon, ordinary oxygen) or bulb pressure (labeled oxygen). Et$_2$Hg was added neat by calibrated syringe through the septum. Solid Ph$_2$Hg was added through the gas inlet port by opening it briefly. Reaction was considered to be over with the disappearance of the color of Th^{+}·. In the case of Ph$_2$Hg this took several days, while in the case of Et$_2$Hg it occurred immediately when Et$_2$Hg was introduced. Five milliliters of the reaction solution was removed, and all volatile liquids were pumped off and trapped in liquid nitrogen. The trapped fluid was used for the search and assay of benzene (Ph$_2$Hg), acetaldehyde, and ethanol (Et$_2$Hg) by GLC. The residue remaining from the 5-mL sample was combined with the untreated 25 mL of solution, and the whole was worked up mainly as described earlier.[4] Briefly, this consisted of pouring the solution into 200 mL of aqueous lithium chloride (0.7 g) and extracting all organics into methylene chloride which was then dried and evaporated. In the Ph$_2$Hg cases the weighed residue was chromatographed on neutral alumina (Woelm activity I, No. 402135) to give (eluant): Th (cyclohexane), ThO (cyclohexane/methylene chloride, 20:80), PhHgCl (methylene chloride), and ThPh$^+$ClO$_4^-$ (methanol). In the Et$_2$Hg cases the ThEt$^+$ClO$_4^-$ was unstable to column chromatography. Therefore, the weighed residue was dissolved in 10 mL of methylene chloride, and 80 mL of dry ether was added to precipitate ThEt$^+$ClO$_4^-$. The filtrate from this was then evaporated, and the weighed residue was again chromatographed to give (eluant): Th (cyclohexane), ThO (petroleum ether/methanol, 95:5), and EtHgCl (methanol). All solid products were checked and characterized by TLC and melting point. Acetaldehyde and ethanol (Et$_2$Hg under oxygen) were assayed in run 2 with a 10-ft column of Carbowax 20M (0.8%) on 60–80-mesh Chromasorb P. The assays were 0.24 mmol of CH$_3$CHO and 0.75 mmol of CH$_3$CH$_2$OH, representing, respectively, 11.5% and 36% of the ethyl radicals that could be formed (eq 9). The formation of thianthrene 5,10-dioxide (ThO$_2$) in reactions of Et$_2$Hg was confirmed by mass spectrometry and comparison (TLC) with authentic ThO$_2$, mp 280 °C. The search for phenol in reactions of Ph$_2$Hg was made with the aqueous LiCl solution, using the FeCl$_2$ spot test along with controls, and was negative. Searches for biphenyl and the adduct[24] of phenol to Th^{+}· were made for the Ph$_2$Hg products by TLC with the use of authentic compounds and were negative. Experimental quantities of reactants and of isolated products are listed in Table III.

Acknowledgment. We thank Dr. Frank W. Crow, Midwest Center for Mass Spectrometry (a regional NSF facility), University of Nebraska, Lincoln, NE, for the mass spectrometry of ^{18}O-labeled compounds.

Registry No. Th^{+}·, 34507-27-2; ThEt$^+$·ClO$_4^-$, 65886-49-9; Et$_2$Hg, 627-44-1; Ph$_2$Hg, 587-85-9.

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[21] Evans, B.; Smith, K. *Tetrahedron Lett.* **1977**, 3079.

[22] Zakharkim, L. I.; Okhlobystin, O. Yu. *Dokl. Akad. Nauk SSSR* **1957**, *116*, 236.

[23] Murata, V.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

[24] Kim, K.; Hull, V. J.; Shine, H. J. *J. Org. Chem.* **1974**, *39*, 2534.