

fect, although many reagents were tried. In general, only **16** could be isolated from these attempted oxidations. However, it was possible to acetylate **13** to afford ester **14** (76%), which upon oxidation with NBS yield the aromatized acetate **15** (73%). This compound could be cleanly hydrolyzed and methylated in one step to give eupolauramine (**1**) in 82% yield identical with an authentic sample.¹¹

Acknowledgment. We thank The National Science Foundation for support of this research on Grant CHE81-00132.

Registry No. 1, 58856-98-7; 2, 74272-88-1; 3, 18742-02-4; 4, 84731-36-2; 5, 84731-37-3; 5 aldehyde, 84731-38-4; 6, 84731-39-5; 8, 84731-40-8; 9, 84731-41-9; 10, 84731-42-0; 11, 84731-43-1; 12, 84731-44-2; 13, 84731-45-3; 14, 84731-46-4; 15, 84731-47-5; 16, 84731-48-6; 17, 84731-49-7.

Supplementary Material Available: Listing of physical and spectral data for all new compounds (5 pages). Ordering information is given on any current masthead page.

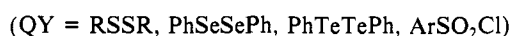
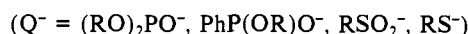
Free-Radical Chain-Substitution Reactions of Alkylmercury Halides¹

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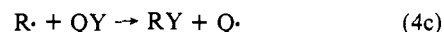
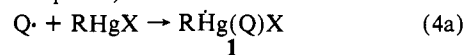
We have previously reported that organomercury halides will participate in free-radical chain-reactions 1-3.^{2,3} Although alkyl (alkyl)HgX + R₂C=NO₂⁻ → (alkyl)C(R)₂NO₂ + Hg⁰ + X⁻ (1)



radicals are involved in reaction 1,⁴ substitution in 1-alkenylmercurials (reactions 2 and 3) does not involve alkenyl radicals since the reaction with Q⁻ = PhS⁻ or QY = PhSSPh proceeds readily in the presence of PhSH to yield the alkenylphenyl sulfide and not the alkene.^{3,5} On the other hand the presently reported reaction 4, which also occurs by a free-radical chain mechanism, quite clearly does involve the alkyl free radical as an intermediate.⁶

Reaction of QY = PhSSPh, PhSeSePh, PhTeTePh, *p*-MePhSO₂SePh, or PhSO₂Cl with alkylmercurials (RHgX, R = Δ⁵-hexenyl, Δ³-butenyl, *n*-hexyl, neopentyl, isopropyl, cyclohexyl, cyclopentylcarbinyl, 7-norbornyl), summarized in Table I, proceeds cleanly in the presence of free-radical chain initiation (*hν*, 25-45 °C; AIBN, 80 °C) to yield RY. Reaction is not observed in the dark in PhH solution while the photostimulated reaction is inhibited by 10 mol % of (Me₃C)₂NO. In the case of the Δ⁵-hexenyl

substituent, extensive cyclization occurs to yield the cyclopentylcarbinyl product. From the yields of uncyclized and cyclized products for Δ⁵-hexenylmercury chloride, the rate constants for the S_H2 attack of the Δ⁵-hexenyl radical upon PhYYPh is calculated to be 7.6 × 10⁴ (Y = S), 1.2 × 10⁷ (Y = Se), and 4.8 × 10⁷ (Y = Te) L/(mol s).⁷ The Δ³-butenylmercury chloride gives no cyclized products.⁸ Further evidence that the free alkyl radical is involved in reaction 4 is provided by the observation that PhSO₂Cl yields RCl and no PhSO₂R, *p*-MePhSO₂SePh yields only RSePh, and BrCCl₃ yields 1-bromohexane (56%) with *n*-hexylmercury chloride.⁹ These products are consistent with the mechanism given in eq 4a-c).¹⁰⁻¹² The reaction does not occur



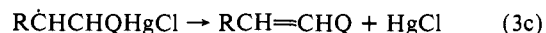
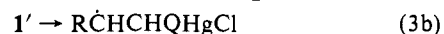
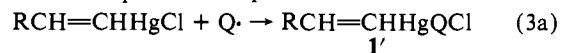
for PhHgX or (cyclopropyl)HgX, presumably because of the high bond-dissociation energies for **1** in reaction 4b. With Δ⁵-hexenyl cyclization, the second-order rate constants for attack of the Δ⁵-hexenyl radical on PhSO₂Cl and *p*-MePhSO₂SePh are found to be 3.7 × 10⁴ and 3.0 × 10⁶ L/(mol s).⁷

A modification of reaction 4 involves the participation of PhSH, either alone or in the presence of PhSSPh (reaction 5). Now



the alkyl radical can be trapped by PhSH to yield RH and PhS (= Q[·]), which continues the chain. Again, Δ⁵-hexenyl gives some cyclized product (methylcyclopentane) from which the value of ~8 × 10⁷ L/(mol s) can be calculated for the hydrogen abstraction reaction of Δ⁵-hexenyl radical with PhSH.¹³

It is interesting to speculate if the observed α attack of radicals Q[·] upon 1-alkenylmercurials³ involves **1'** as an intermediate (eq 3a-d). Such an explanation is quite consistent with the obser-



vation that an unsymmetrical reagent QY such as PhSO₂Cl yields only the sulfone (RQ) in reaction 3 but only the alkyl chloride (RY) in reaction 4.

The reactions of benzylmercurials took a somewhat different course than the reactions of primary alkylmercurials in that significant yields of bibenzyl were often observed. Furthermore, the bibenzyl must be formed by a chain process since 5-10 mol % of (Me₃C)₂NO[·] inhibited these reactions for extended periods of time. Photostimulated reaction of PhCH₂HgCl with 1 equiv

(7) Based on a unimolecular cyclization rate constant of 1 × 10⁵ s⁻¹ for the Δ⁵-hexenyl radical (Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317).

(8) Free-radical reactions leading to cyclopropylcarbinyl products have been reported for homoallylcobalt compounds: Ashcroft, M. R.; Bury, A.; Cooksey, C. J.; Davies, A. G.; Gupta, B. D.; Johnson, M. D.; Morris, H. J. *Organomet. Chem.* **1980**, *195*, 89.

(9) *n*-Alkylmercury chlorides or (*n*-Bu)₂Hg react with CCl₃ to give alkyl radicals with little involvement of the elimination reaction observed for certain dialkylmercurials by Nugent and Kochi: Nugent, W. A.; Kochi, J. K. *J. Organomet. Chem.* **1977**, *124*, 327.

(10) The S_H2 reaction, R[·] + PhSHgR' → PhSR + HgR', has been observed for R = *i*-Pr, R' = Ph and for R = R' = *n*-Bu. However, PhSSPh is much more reactive than PhSHgBu and undoubtedly more reactive than PhSHgCl in this process.

(11) The reaction of RHgX with polyhaloalkanes in the presence of NaBH₄ to yield RCl or RBr apparently involves the reaction sequence 4a-c among other processes: Giese, B. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 173, 174.

(12) Racemization of chiral organomercurials by a free-radical chain quite likely proceeds by reactions 4a,b; for pertinent references see: Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968.

(13) Electrophilic cleavage of the Δ⁵-hexenyl moiety by PhSH is discounted because of the total inhibition of the reaction by (Me₃C)₂NO[·] (Table I).

(1) Supported by Grant CHE-8119343 from the National Science Foundation and a scholarship to H. T. from Yarmouk University, Irbid, Jordan.

(2) Russell, G. A.; Hershberger, J.; Owens, K. *J. Am. Chem. Soc.* **1979**, *101*, 1312.

(3) Russell, G. A.; Hershberger, J. *J. Am. Chem. Soc.* **1980**, *102*, 7603.

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

(5) The phenyl radical abstracts hydrogen from PhSH at an essentially diffusion-controlled rate (Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589) while a primary alkyl radical abstracts hydrogen from PhSH ~20 times as readily as S_H2 attack on PhSSPh and has essentially no reactivity toward PhS⁻ (unpublished results with J. Tanko).

(6) The thermal reaction of PhSeSePh and PhTeTePh with dialkylmercurials has been reported without mechanistic interpretation: Okamoto, Y.; Yano, T. *J. Organomet. Chem.* **1971**, *29*, 99.

Table I. Photostimulated Reaction, $\text{RHgCl} + \text{QY} \rightarrow \text{RY} + \text{ClHgQ}$

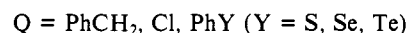
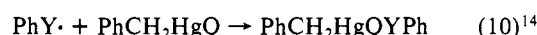
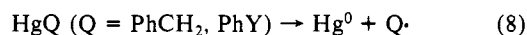
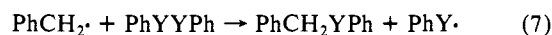
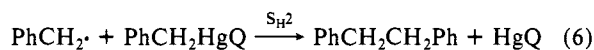
R	Q-Y	conditions ^a	RY, % ^b
$\text{CH}_2=\text{CHCH}_2\text{CH}_2$	PhS-SPh	PhH, 4 h	92
$\text{CH}_2=\text{CHCH}_2\text{CH}_2$	PhS-SPh	PhH, dark, 6.5 h, 50 °C	0
$\text{CH}_2=\text{CHCH}_2\text{CH}_2$	PhS-SPh	PhH, 4 h, 10 mol % $(\text{Me}_3\text{C})_2\text{NO}\cdot$	0
$\text{CH}_2=\text{CHCH}_2\text{CH}_2$	PhS-SPh	PhH, AIBN, 10 h, 80 °C	64 ^c
$\text{CH}_2=\text{CHCH}_2\text{CH}_2$	PhSe-SePh	PhH, 5 h	85
$\text{CH}_2=\text{CHCH}_2\text{CH}_2$	PhTe-TePh	PhH, 3 h	92
$\text{CH}_2=\text{CHCH}_2\text{CH}_2$	<i>p</i> -MePhSO ₂ - SePh	PhH, 4 h	87
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2$	PhS-SPh	PhH, 3 h	78
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2$	PhSe-SePh	PhH, 4 h	82
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2$	PhTe-TePh	PhH, 4 h	83
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2$	<i>p</i> -MePhSO ₂ - SePh	PhH, 5 h	82
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2$	PhSO ₂ -Cl	PhH, 48 h ^d	46
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2$	CCl ₃ -Br	PhH, 36 h	56
$(\text{CH}_3)_3\text{CCH}_2$	PhS-SPh	PhH, 12 h	74
$(\text{CH}_3)_3\text{CCH}_2$	PhSe-SePh	PhH, 5 h	86
$(\text{CH}_3)_3\text{CCH}_2$	PhTe-TePh	PhH, 6 h	78
$(\text{CH}_3)_3\text{CCH}_2$	<i>p</i> -MePhSO ₂ - SePh	PhH, 10 h	75
$(\text{CH}_3)_2\text{CH}$	PhS-SPh	PhH, 4 h	100
$(\text{CH}_3)_2\text{CH}$	PhSe-SePh	PhH, 5 h	100
cyclo-C ₆ H ₁₁	PhS-SPh	Me ₂ SO, 18 h	65 ^c
cyclo-C ₆ H ₁₁	PhSe-SePh	Me ₂ SO, 16 h	72 ^c
cyclo-C ₆ H ₉ CH ₂	PhS-SPh	PhH, 4 h	86 (73 ^c)
cyclo-C ₆ H ₉ CH ₂	PhSe-SePh	PhH, 4 h	84
7-norbornyl	PhS-SPh	PhH, 6 h	43 ^e
7-norbornyl	PhSe-SePh	PhH, 4 h	53 ^e
7-norbornyl	PhTe-TePh	PhH, 10 h	45 ^e
7-norbornyl	<i>p</i> -MePhSO ₂ - SePh	PhH, 10 h	48 ^e
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2$	PhS-S-Ph	PhH, 3 h	88 ^f
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2$	PhSe-SePh	PhH, 3 h	93 ^f
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2$	PhTe-TePh	PhH, 8 h	85 ^f
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2$	<i>p</i> -MePhSO ₂ - SePh	PhH, 6 h	81 ^f
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2$	PhSO ₂ -Cl	PhH, 48 h ^d	54 ^f
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2$	PhS-H	PhH, 5 h	58 ^f
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2$	PhS-H	PhH, dark, 10 mol % $(\text{Me}_3\text{C})_2\text{NO}\cdot$, 30 °C, 38 h	0
PhCH ₂	PhS-SPh	PhH, 4 h ^d	15 (66 ^g)
PhCH ₂	PhSe-SePh	PhH, 2 h	72 (7 ^g)
PhCH ₂	PhTe-TePh	PhH, 1 h	80 (0 ^g)
PhCH ₂	<i>p</i> -MePhSO ₂ - SePh	PhH, 6 h	68 (5 ^g)
PhCH ₂ ^h	PhS-SPh	PhH, 6 h ^d	8 (72 ^g)
PhCH ₂ ^h	PhTe-TePh	PhH, 1 h	100 (0 ^g)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ ^h	PhS-SPh	PhH, 2.5 h	100
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ ⁱ	PhS-SPh	PhH, 21 h	85

^a In a typical experiment RHgCl (1 mmol) and QY (1.2 mmol) in 10 mL of solvent were irradiated with a 275-W sunlamp approximately 15 cm from the Pyrex reaction flask. The reaction temperature was ~45 °C. ^b ¹H NMR yield. ^c Isolated yield (5-mmol scale). ^d Irradiated in a Rayonet reactor (350 nm). ^e RHgBr reactant. A significant amount of RR was recovered. ^f Mixture of R = Δ^5 -hexenyl and cyclopentylcarbinyl whose ratio (GLPC) was dependent on the concentration of QY. ^g Yield of PhCH₂CH₂Ph. ^h RHgX = R₂Hg (1 mmol); QY (2 mmol). ⁱ Bu₂Hg (1 mmol) and PhSSPh (1.2 mmol) yielded 1.7 mmol of PhSBu.

of PhSSPh yielded mainly PhCH₂CH₂Ph and PhSHgCl while the better radical traps PhSeSePh or PhTeTePh led mainly to PhCH₂SePh and exclusively to PhCH₂TePh (Table I). Dibenzylmercury undergoes a facile photostimulated decomposition (inhibited by $(\text{Me}_3\text{C})_2\text{NO}\cdot$) to PhCH₂CH₂Ph and Hg⁰ while PhCH₂HgSPh undergoes a photostimulated chain decomposition yielding PhCH₂CH₂Ph, (PhS)₂Hg, and Hg⁰. Benzylmercury chloride does not readily undergo a chain decomposition, but in the presence of anions (A⁻), which promote the symmetrization to $(\text{PhCH}_2)_2\text{Hg}$ and $\text{HgCl}_2\text{-A}^-$ (A⁻ = (EtO)₂PO⁻, ArSO₂⁻, NO₂⁻),

photostimulated decomposition occurs.⁴ Bibenzyl could be formed in these processes by the S_H2 attack of benzyl radical at the benzyl carbon of the mercurial or by decomposition of the Hg^{III} intermediate $(\text{PhCH}_2)_2\text{HgQ}$, 1'' (Q = PhCH₂, Cl, SPh, SePh, TePh). To distinguish between these alternatives, we have studied the chain reactions between $(\text{PhCH}_2)_2\text{Hg}$ and PhYYPh (Y = S, Te) in which addition of PhY· to $(\text{PhCH}_2)_2\text{Hg}$ would produce 1'' with Q = PhS or PhTe. Reaction of 2 equiv of PhTeTePh with $(\text{PhCH}_2)_2\text{Hg}$ proceeded rapidly when photostimulated to yield quantitatively PhCH₂TePh and $(\text{PhTe})_2\text{Hg}$. We conclude that decomposition of 1'' (Q = PhTe) leads to the benzyl radical and not directly to bibenzyl. With PhSSPh (2 equiv), a poorer trap for PhCH₂· than PhTeTePh, the major reaction product was PhCH₂CH₂Ph (Table I). We thus conclude that bibenzyl is formed by attack of PhCH₂· at the benzyl position of a carbon-mercury bond with $k_6 > k_7$ for Y = S but $k_7 > k_6$ for Y = Te (Scheme I).

Scheme I



Acknowledgment. Samples of cyclopropyl- and 7-norbornylmercury bromide were kindly supplied by Professor B. Giese.¹¹

Registry No. $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{HgCl}$, 14660-38-9; $\text{CH}_3(\text{CH}_2)_4\text{C}-\text{H}_2\text{HgCl}$, 17774-09-3; $(\text{CH}_3)_3\text{CCH}_2\text{HgCl}$, 10284-47-6; $(\text{CH}_3)_2\text{CHHgCl}$, 30615-19-1; *c*-C₆H₁₁HgCl, 24371-94-6; *c*-C₆H₉CH₂HgCl, 33631-66-2; 7-norbornyl HgCl, 84649-28-5; $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2\text{HgCl}$, 63668-13-3; PhCH₂HgCl, 2117-39-7; PhSSPh, 882-33-7; PhSeSePh, 1666-13-3; PhTeTePh, 32294-60-3; *p*-MePhSO₂SePh, 68819-94-3; PhSO₂Cl, 98-09-9.

(14) S_H2 attack of PhY· at the carbon of PhCH₂HgQ or decomposition of PhCH₂HgQYPh directly to PhCH₂HgQYPh are discounted because of the cyclization observed in the reactions of Δ^5 -hexenylmercurials.

Iron Porphyrin Dependent Oxidation of Methyl- and Phenylhydrazine: Isolation of Iron(II)-Diazene and σ -Alkyliron(III) (or Aryliron(III)) Complexes. Relevance to the Reactions of Hemoproteins with Hydrazines

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Monosubstituted hydrazines, particularly arylhydrazines, have been shown to react with several hemoproteins such as hemoglobin¹ (Hb), myoglobin² (Mb), cytochrome P-450,³ lactoperoxidase,⁴ and horseradish peroxidase,⁵ forming heme adducts and producing a partial inhibition or destruction of these hemoproteins.⁶ The

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