H), 7.42 (d of t, $J = 8.5$, 1.4 Hz, 1 H), 4.44 (q, $J = 7.2$ Hz, CH_2), 2.56 (s, CH_3), and 1.50 (t, $J = 7.2$ Hz, CH_3). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 175.08, 170.74, 132.49, 131.24, 129.39, 129.35, 126.04, 124.22, 122.63, 121.00, 120.90, 118.49, 101.90, 36.82, 20.73, and 14.78. IR (KBr): 1650 (C=O) cm^{-1}. MS: *m/e* 254 (18, M + 1), 253 (100, M), 235 (38), 220 (16), 188 (10), 168 (18), 167 (11). Mp: 139.5–140.5 °C. Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.86; H, 5.95; N, 5.45.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation for this work and for partial funding for the mass spectrometer and NMR spectrometers employed in these investigations. Partial funding for the high-field NMR spectrometer was also obtained from the Keck Foundation. We thank the Johnson Matthey Co. for their loan of rhodium(III) chloride.

Registry No. **3a**, 38118-69-3; **3b**, 112482-66-3; **3d**, 112482-67-4; **3e**, 112482-68-5; **3f**, 112482-69-6; **3g**, 112482-70-9; **4a**, 38118-70-6; **4b**, 112482-71-0; **4c**, 112482-72-1; **4d**, 112482-73-2; **4e**, 112482-74-3; **4f**, 112482-75-4; **4g**, 112482-76-5; **5** (Z = H), 61-70-1; **5** (Z = Ac), 59624-50-9; **6** (Z = H), 7135-32-2; **6** (Z = Ac), 112482-84-5; **7** (Z = H), 112482-77-6; **8** (Z = H), 112482-78-7; **8** (Z = Ac), 112482-85-6; **9a** (Z = H), 112482-79-8; **9a** (Z = Ac), 112482-86-7; **9b** (Z = H), 112482-80-1; **9b** (Z = Ac), 112482-87-8; **10a** (Z = H), 112482-81-2; **10a** (Z = Ac), 112482-88-9; **10b** (Z = H), 112482-82-3; **10b** (Z = Ac), 112482-89-0; **11** (Z = H), 112482-83-4; **11** (Z = Ac), 112482-90-3; Ph_2NH, 122-39-4; PhNHMe, 100-61-8; PhNHBen, 103-32-2; Me-*o*-C_6H_4NHEt, 94-68-8; 2,3-$Me_2C_6H_3$NHEt, 41115-23-5; Me-*m*-C_6H_4NHEt, 102-27-2; 3,4-$CH_2(O_2)C_6H_3$NHEt, 32953-14-3; $MeSO_2N_3$, 1516-70-7; α-naphthyl-NHEt, 118-44-5; diketene, 674-82-8.

Metal–Metal Exchange of α-Metallo Ketones. Novel Formation of α-Acyl Anion and α-Keto Carbonium Ion Equivalents from (Aryl)phenacyl Tl^{III}, Pb^{IV}, and Hg^{II} Systems

Robert M. Moriarty,* Raju Penmasta, Indra Prakash, and Alok K. Awasthi

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

Received April 8, 1987

The novel class of α-metallo ketones $RCOCH_2Tl^{III}$tolyl($OCOCF_3$) where R = phenyl, substituted phenyl, thienyl, pyridinyl, and *tert*-butyl have been synthesized and characterized by ^1H NMR and ^{13}C NMR. These compounds serve as anion equivalents in the $TiCl_4$-mediated aldol condensation. Metal–metal exchange with iodosylbenzene or lead tetraacetate leads to α-nucleophilic substitution derived from the formal α-keto carbonium ion equivalent. The corresponding p-$CH_3OC_6H_4COCH_2Pb^{IV}C_6H_4OCH_3$-$p$-$(OCOCH_3)_2$ and $(p\text{-}CH_3OC_6H_4COCH_2)_2Hg^{II}$ analogues were synthesized and shown to likewise behave as either enolate anion or α-keto carbonium ion equivalents upon metal–metal exchange with Ti^{IV}, Pb^{IV}, or I^{III}. The importance of this work is that the range of reactivity of α-metallo ketones may be selectively adjusted by metal–metal or metal–metalloid exchange.

α-Metallo ketones, also known as α-metalloacyl systems, -MCH_2CO-, have been well studied for group IVA acylsilanes, acylgermanes, and acylstannanes.[1] Carbon to oxygen rearrangement is a primary process for these compounds. In the cases of silicon[2] and tin[1b,3] both isomers have been studied separately. Among group IIB elements α-mercurio ketones have been used in the aldol condensation.[4] Even though Hg(II) can show redox behavior, -$HgCR_2CO$- acts as an anion equivalent. Hypervalent iodine can occur in systems of the type -MCH_2CO- where M = I^{III} as in $RCOCH_2I^{III}C_6H_5X$[5] and $(RCO)_2C^{-+}IC_6H_5$;[6] however, in these cases the invariable course of chemical reaction is reductive elimination of $C_6H_5I^I$ with overall nucleophilic substitution at carbon. The chemistry of organoiodine(III) compounds such as $C_6H_5I^{III}X_2$ is similar to that of $Pb^{IV}X_4$,[7] $Tl^{III}X_3$,[8] and $Hg^{II}X_2$,[9] the common reactivity pattern is reductive elimination, i.e., $Pb^{IV} \rightarrow Pb^{II}$, $Tl^{III} \rightarrow Tl^{I}$, and $Hg^{II} \rightarrow Hg^0$ with Pb^{IV} being the most easily reduced (−1.6 V) and Hg^{II} the least easily reduced (−0.92 V). Pursuant to these formal relationships we synthesized the α-metallo ketones corresponding to these three redox metals, namely, $RCOCH_2M(OCOR)_n(Ar)$, where M = Tl^{III}, Pb^{IV}, and Hg^{II}, **2a–f**, **3**, and **4**, respectively, with the objective of comparing their chemistry with that of the related $RCOCH_2I^{III}C_6H_5X$ mentioned above. We now report

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(1) (a) For a review, see: Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 96. The term "β-ketometalloid" used by Brook in this chapter is acknowledged to be confusing. In a conventional organic chemical designation a β-keto metalloid would be thought of as -MCH_2CH_2COR while emphasis on the metal atom accounts for the β-keto metalloid nomenclature. (b) Odic, Y.; Pereyre, M. *J. Organomet. Chem.* **1973**, *55*, 273.

(2) (a) The stereochemistry of this process in the case of β-keto silanes has been studied in Brook et al. Brook, A. G.; Mac Rae, D. M.; Limburg, R. W. *J. Am. Chem. Soc.* **1967**, *89*, 5493. (b) Lutsenko, I. F.; Baukov, Y. I.; Dudukina, O. V.; Kramarova, E. N. *J. Organomet. Chem.* **1968**, *11*, 35. (c) Matsuda, I.; Sato, S.; Hattori, M.; Izumi, Y. *Tetrahedron Lett.* **1985**, *26*, 3215.

(3) (a) Pereyre, M. "Recherches sur les Reactions d'Hydures Organostanniques avec des Systêmes non Sature", Dissertation, Bordeaux, 1965, p 133. (b) Pereyre, M.; Bellegarde, B.; Mendelsohn, J.; Valade, J. *J. Organomet. Chem.* **1968**, *11*, 97.

(4) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1982**, *104*, 2323.

(5) For a discussion of this intermediate, see: Moriarty, R. M.; Prakash, O.; Duncan, M. P. *Synthesis* **1985**, 943.

(6) These compounds, called iodonium ylides, react with HX to yield the protonated form which reacts further with X^- with the reductive elimination of C_6H_5I. For a discussion of the protonolysis of iodinanes with Brønsted acids, see: Koser, G. F. In *The Chemistry of Functional Groups*, Supplements D; Patai, S.; Rappaport, S., Eds.; Wiley: New York, 1983; Chapter 18, pp 790–792.

(7) (a) For a comparison of iodosobenzene with $Pb(OAc)_4$, see: Bunton, C. A. In *Oxidations in Organic Chemistry*, Part A, Wiberg, K. B., Ed.; Academic Press: New York and London, 1965; pp 367–433. (b) Reference 7a, Criegee, R., 1965; pp 278–365.

(8) McKillop, A., Taylor, E. C. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: England, 1982; Vol. 7, pp 465–513.

(9) Negishi, E. *Organometallics in Organic Synthesis*; John Wiley and Sons: New York, 1980; Vol. 1, pp 455–479.

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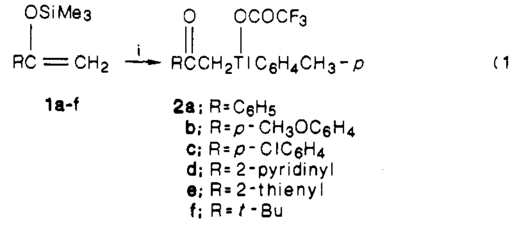
Table I. Protonolysis of $RCOCH_2M(OCOR')_n$ with CF_3COOH (M = Tl^{III}, Pb^{IV}, and Hg^{II})

α-metallo ketone $RCOCH_2M(OCOR')$, R′ = CH_3 or CF_3	product[a] obtained	yield (%)
2a	$C_6H_5COCH_3$	83
2b	p-$CH_3OC_6H_4COCH_3$	85
2c	p-$ClC_6H_4COCH_3$	85
4	p-$CH_3OC_6H_4COCH_3$	90

[a] All the compounds were characterized by their IR and NMR spectra and were compared with the literature NMR spectra collection of Aldrich.

that (a) these α-metallo ketones act as anion equivalents as in protonolysis, (b) they behave as anionic components in the $TiCl_4$ aldol condensation via metal–metal exchange with $TiCl_4$, and (c) they act as a α-keto carbonium ion equivalents via metal–metal exchange with $Pb^{IV}(OAc)_4$ or $(C_6H_5I^{III}O)_n$. Thus (aryl)phenacyl metals are *anion equivalents*, or upon appropriate metal–metal exchange they can act as *α-keto carbonium ion equivalents*.

The series of novel (para-substituted phenacyl)-p-tolylthallium(III) trifluoroacetates **2a–c**, pyridinyl **2d**, and thienyl **2e** compounds as well as the aliphatic *tert*-butyl **2f** examples were synthesized as shown in eq 1.



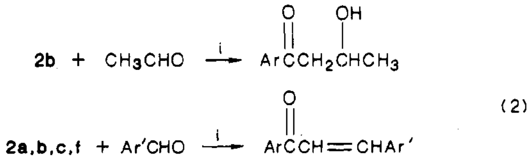
$$RC(OSiMe_3)=CH_2 \xrightarrow{i} RC(=O)CH_2Tl(OCOCF_3)C_6H_4CH_3\text{-}p \qquad (1)$$

1a-f **2a**; R = C_6H_5
b; R = p-$CH_3OC_6H_4$
c; R = p-ClC_6H_4
d; R = 2-pyridinyl
e; R = 2-thienyl
f; R = t-Bu

(i) p-$CH_3C_6H_4Tl(OCOCF_3)_2/C_6H_6$, room temperature

Products **2a–f** are stable crystalline solids which precipitate directly from the reaction solution. The structures are based, inter alia, upon ^1H NMR, particularly J_{Tl-CH_2} = 773 Hz for **2a**, 765 Hz for **2b**, and 794 Hz for **2c**.[10] These values exclude the isomeric enol structure and this point was also established in the case of a deuterio analogue of **2a**. The values of J_{Tl-CH_2} in the ^{13}C NMR for **2a**, **2b**, and **2c** are also characteristic, i.e. 2634 Hz, 2653 Hz, and 2946 Hz, respectively.

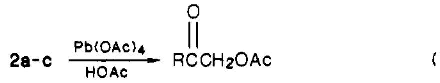
That **2a**, **2b**, and **2c** behave as anion equivalents was shown by protonolysis with CF_3CO_2H to form the acetophenone and p-$CH_3C_6H_4Tl(OCOCF_3)_2$ in high yield (Table I). This result is unexpected since C_{sp^3}–Tl^{III} bonds characteristically cleave with reductive elimination, i.e. $Tl^{III} \rightarrow Tl^{I}$. The protonolysis result prompted us to study **2a–f** as anion components in the aldol condensation. Various Lewis acids ($BF_3 \cdot OEt_2$, $SnCl_4$, Bu_4NF) were not useful in effecting the addition of **2a–f** with aldehydes but $TiCl_4$ gave good yields of the aldol products (eq 2, Table II).



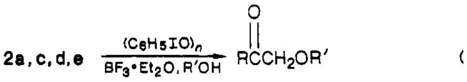
$$\mathbf{2b} + CH_3CHO \xrightarrow{i} ArC(=O)CH_2CH(OH)CH_3$$
$$\mathbf{2a,b,c,f} + Ar'CHO \xrightarrow{i} ArC(=O)CH{=}CHAr' \qquad (2)$$

(i) $TiCl_4$/-78°; THF

Since a stoichiometric quantity of $TiCl_4$ was required and the characteristic red color for organo-Ti^{IV} species was observed as well as consonant ^1H NMR indications we propose metal–metal exchange to form a titanium enolate.[11] This result led us to investigate other metal–metal exchange reactions which might proceed with reductive elimination and overall oxidative α-nucleophilic substitution. This type reaction was realized in two different systems, namely, metal–metal exchange in the case of $Pb(OAc)_4$ (eq 3) and metal–metalloid exchange in the case of $(C_6H_5IO)_n$ (eq 4). The yields of α-alkoxy ketones (Table IV) and α-acetoxy ketones (Table III) are excellent.

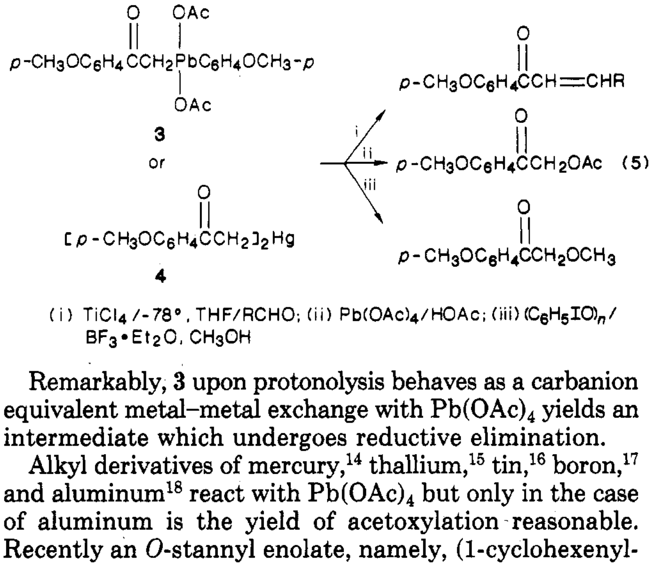


$$\mathbf{2a\text{-}c} \xrightarrow[HOAc]{Pb(OAc)_4} RC(=O)CH_2OAc \qquad (3)$$



$$\mathbf{2a,c,d,e} \xrightarrow[BF_3 \cdot Et_2O,\ R'OH]{(C_6H_5IO)_n} RC(=O)CH_2OR' \qquad (4)$$

Having established protonolysis and metal–metal or metal–metalloid exchange for **2a–f**, we turned our attention to analogous α-phenacyl Pb^{IV} [12] and di(α-phenacyl)-Hg^{II} [13] systems in order to determine whether comparable behavior might occur. Indeed **3** and **4** (eq 5) undergo protonolysis, aldol condensation via exchange with $TiCl_4$, and oxidative substitution with $Pb(OAc)_4$ and $(C_6H_5IO)_n$ just as was observed for **2a–f**.



(i) $TiCl_4$/-78°, THF/RCHO; (ii) $Pb(OAc)_4/HOAc$; (iii) $(C_6H_5IO)_n/BF_3 \cdot Et_2O$, CH_3OH

Remarkably, **3** upon protonolysis behaves as a carbanion equivalent metal–metal exchange with $Pb(OAc)_4$ yields an intermediate which undergoes reductive elimination.

Alkyl derivatives of mercury,[14] thallium,[15] tin,[16] boron,[17] and aluminum[18] react with $Pb(OAc)_4$ but only in the case of aluminum is the yield of acetoxylation reasonable. Recently an O-stannyl enolate, namely, (1-cyclohexenyloxy)tetraethyltin was oxidized with $Pb(OAc)_4$ to yield the α-acetoxy ketone, dimer, and cyclohexanone.[19]

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[10] (a) Maher, J. P.; Evans, D. F. *Proc. Chem. Soc.* **1961**, 208. (b) Maher, J. P.; Evans, D. F. *Proc. Chem. Soc.* **1963**, 176. (c) Maher, J. P.; Evans, D. F. *J. Chem. Soc.* **1963**, 5534. (d) McKillop, A.; Fowler, J. S.; Zelesko, M. J.; Hunt, J. D. *Tetrahedron Lett.* **1969**, 2423.

[11] Titanium homoenolates have been isolated (Nakamura, E.; Kuwajime, I. *J. Am. Chem. Soc.* **1983**, *105*, 651) and studied (Goswami, R. *J. Org. Chem.* **1985**, *50*, 5909). Baker, W. R. *J. Org. Chem.* **1985**, *50*, 3943. For recent reviews of organotitanium chemistry, see: (a) Reetz, M. *Top. Curr. Chem.* **1982**, *1*, 106. Weidman, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31. In a ^1H NMR experiment **2a** was dissolved in THF-d_8 and cooled to –60 °C; then addition of $TiCl_4$ as a neat liquid and slow annealing to room temperature led to disappearance of the CH_2-Tl peaks and characteristic shifts $C_6H_4CH_3$-p resonances consistant with exchange of $Tl(OCOCF_3)$(tolyl) for $TiCl_3$.

[12] Bell, H. C.; Pinhey, J. T.; Sternhill, S. *Aust. J. Chem.* **1982**, *35*, 2237.

[13] House, H. O.; Auerbach, R. A.; Gall, R. A.; Peet, N. P. *J. Org. Chem.* **1973**, *38*, 514.

[14] (a) Criegee, R.; Dimroth, P.; Schempf, R. *Chem. Ber.* **1957**, *90*, 1337. (b) Kabbe, H. J. *Justus Liebigs. Ann. Chem.* **1962**, *656*, 204. (c) Kampel, V. T.; Bilevitch, K. A.; Okhlobystin, O. Y. *Dokl. Akad. Nauk. SSSR* **1971**, *197*, 95.

[15] Taylor, E. C.; Altland, H. W.; Danforth, R. H.; McGillivray, G.; McKillop, A. *J. Am. Chem. Soc.* **1970**, *92*, 3520.

[16] Christen, U.; Neumann, W. P. *J. Organomet. Chem.* **1972**, *39*, 58.

[17] Matsuda, Y.; Arase, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 901.

[18] Sato, F.; Mosy, Y.; Sato, M. *Tetrahedron Lett.* **1979**, 1405.

[19] Kashin, A. N.; Tulchinskii, M. L.; Bumagin, N. A.; Beletskaya, I. P. Reutov, O. A. *Zh. Org. Khim.* **1982**, *18*, 1588.

Table II. Aldol Condensation of $RCOCH_2M(OCOR')_n$ with Carbonyl Compounds (M = Tl^{III}, Pb^{IV}, and Hg^{II})

α-metallo ketone $RCOCH_2M$-$(OCOR')$, R′ = CH_3 or CF_3	aldehyde or ketone	product[a] obtained	yield (%)	mp (lit. mp),[23] °C
2a	p-$CH_3OC_6H_4CHO$	$C_6H_5COCH{=}CHC_6H_4OCH_3$-p[b]	72	77–78 (79)[23a]
2b	CH_3CHO	p-$CH_3OC_6H_4COCH_2CH(OH)CH_3$[c]	70	oil[23b]
2b	2,4-$(CH_3O)_2C_6H_3CHO$	2,4-$(CH_3O)_2C_6H_3CH{=}CHCOC_6H_4OCH_3$-p[b]	80	86–88 (86.5–87.5)[23c]
2b	CH_3COCH_3	p-$CH_3OC_6H_4COCH{=}C(CH_3)_2$[d]	60	oil[23d]
2c	p-$CH_3OC_6H_4CHO$	p-$ClC_6H_4COCH{=}CHC_6H_4OCH_3$-p[b]	78	126–128 (128)[23e]
2f	p-$CH_3OC_6H_4CHO$	$(CH_3)_3CCOCH{=}CHC_6H_4OCH_3$-p[b]	50	oil[23f]
3	CH_3CHO	p-$CH_3OC_6H_4COCH{=}CHCH_3$[c]	60	oil[23g]
3	p-$CH_3OC_6H_4CHO$	p-$CH_3OC_6H_4COCH{=}CHC_6H_4OCH_3$-p[b]	52	96–99 (97–99)[23h]
4	p-$CH_3OC_6H_4CHO$	p-$CH_3OC_6H_4COCH{=}CHC_6H_4OCH_3$-p[b]	50	98–99 (97–99)[23h]

[a] All compounds were purified by column chromatography on silica gel. [b] Using first CH_2Cl_2 and then $CHCl_3$. [c] First CH_2Cl_2 and then ether as eluent. [d] CH_2Cl_2/*n*-hexane (1:1) was used.

Table III. α-Acetoxylation by the Displacement Reactions of α-Metallo Ketone with Lead Tetracetate in Acetic Acid (M = Tl^{III}, Pb^{IV}, and Hg^{II})

α-metallo ketones $RCOCH_2M(OCOR')$, (R′ = CH_3 or CF_3	product	yield (%)	mp (lit.[24] mp), °C
2a	$C_6H_5COCH_2OAc$	83	48–50 (49–50)
2b	p-$CH_3OC_6H_4COCH_2OAc$	85	58–59 (59)
2c	p-$ClC_6H_4COCH_2OAc$	85	65–66 (65.5–66.5)
3	p-$CH_3OC_6H_4COCH_2OAc$	88	58–59 (59)
4	p-$CH_3OC_6H_4COCH_2OAc$	90	57–59 (59)

The central feature in the chemistry of the $RCOCH_2MArX_n$ systems is the retention of the higher oxidation state of the metal, i.e., Tl^{III}, Pb^{IV}, and Hg^{II} both in protonolysis and metal–metal exchange. The aryl group attached to the metal is an influential factor possibly via stabilization involving a σ–π conjugative interaction between the C–M bond and the carbonyl group.[20]

Obvious areas of future interest are the radical reactions of these compounds and the stereochemistry of aldol reactions involving prostereogenic substrates.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Unicam SP1000 IR spectrophotometer. ^1H NMR spectra were recorded at 60 MHz on a Varian A60 or EM-360 spectrometer using TMS as an internal standard. A Bruker WP-250 was used to record ^{13}C NMR spectra. Mass spectra were scanned on a Hewlett Packard GC-MS 5985 spectrometer. Microanalyses were performed by Microtech Labs, Skokie, IL.

Trimethylsilyl Enol Ethers. Trimethylsilyl enol ethers were synthesized by using the method of House et al.[21] and were purified by distillation before use.

***p*-Tolylthallium(III) Bis(trifluoroacetate).** This compound was synthesized from toluene and thallium(III) trifluoroacetate by the method of Bell et al.[22]

General Procedure for the Preparation of α-Thallated Ketones 2a–f. *p*-Tolylthallium(III) bis(trifluoroacetate) (10 mmol) was added to the trimethylsilyl enol ether (15 mmol) in dry benzene (20 mL), and the mixture was shaken until all the solid had dissolved. The clear solution was kept at room temperature for 30 min. The precipitated solid was filtered, washed with benzene, and crystallized from methanol to give α-thallated ketone as colorless crystals. Compounds **2a–f** had the following properties.

2a: mp 245–260 °C (85%); IR (KBr) cm^{-1} 1600–1700 (br); ^1H NMR (DMSO-d_6) δ −3.27 and 9.62 (s, 2 H, CH_2, J_{Tl-CH_2} = 773 Hz), 2.08 and 2.56 (s, 3 H, CH_3, J_{Tl-CH_3} = 29 Hz), 3.93 and 11.42 (m, 2 H, $J_{Tl\text{-}o\text{-}H}$ = 449 Hz), 6.20 and 8.35 (m, 2 H, $J_{Tl\text{-}m\text{-}H}$ = 129 Hz), 7.14–8.21 (m, 5 H, aromatic protons); ^{13}C NMR (DMSO-d_6) δ 20.89 (CH_3), 23.46 and 75.81 (J_{Tl-CH_2} = 2634 Hz), 127.76 and 138.64 ($J_{Tl\text{-}o\text{-}C}$ = 547 Hz), 132.14 and 134.67 ($J_{Tl\text{-}m\text{-}C}$ = 127 Hz), 194.80 and 199.72 (J_{Tl-CO} = 248 Hz), 127.89, 128.04, 128.23, 128.39, 132.29, 137.65, 157.97. Anal. Calcd for $C_{17}H_{14}F_3O_3Tl$: C, 38.71; H, 2.66; Tl, 38.71. Found: C, 38.24; H, 2.83; Tl, 38.24.

2b: mp 241–245 °C (80%); IR (KBr) cm^{-1} 1600–1700 (br); ^1H NMR (DMSO-d_6) δ −3.25 and 9.50 (s, 2 H, CH_2, J_{Tl-CH_2} = 765 Hz), 2.07 and 2.57 (s, 3 H, CH_3, J_{Tl-CH_3} = 30 Hz), 3.85 (s, 3 H, OCH_3), 3.90 and 11.35 (m, 2 H, $J_{Tl\text{-}o\text{-}H}$ = 452 Hz), 6.22 and 8.35 (m, 2 H, $J_{Tl\text{-}m\text{-}H}$ = 128 Hz), 6.95 and 7.97 (dd, 4 H, aromatic protons); ^{13}C NMR (DMSO-d_6) δ 21.00 (CH_3), 23.26 and 75.97 (J_{Tl-CH_2} = 2653 Hz), 55.40 (OCH_3), 123.78 and 138.65 ($J_{Tl\text{-}o\text{-}C}$ = 749 Hz), 131.50 and 134.68 ($J_{Tl\text{-}m\text{-}C}$ = 159 Hz), 193.57 and 198.13 (J_{Tl-CO} = 229 Hz), 113.20, 130.63, 157.56, 158.17, 158.81, 162.58. Anal. Calcd for $C_{18}H_{16}F_3O_4Tl$: C, 38.75; H, 2.87; F, 10.23; Tl, 36.67. Found: C, 38.68; H, 2.70; F, 10.38; Tl, 36.45.

2c: 280–290 °C (75%); IR (KBr) cm^{-1} 1600–1700 (br); ^1H NMR (DMSO-d_6) δ −3.41 and 9.83 (s, 2 H, CH_2, J_{Tl-CH_2} = 794 Hz), 2.05 and 2.53 (s, 3 H, CH_3, J_{Tl-CH_3} = 29 Hz), 3.92 and 11.35 (m, 2 H, $J_{Tl\text{-}o\text{-}H}$ = 446 Hz), 6.17 and 8.34 (m, 2 H, $J_{Tl\text{-}m\text{-}H}$ = 130 Hz), 7.47 and 8.05 (dd, 4 H, aromatic protons); ^{13}C NMR (DMSO-d_6) δ 20.93 (CH_3), 21.64 and 80.19 (J_{Tl-CH_2} = 2946 Hz), 124.31 and 139.00 ($J_{Tl\text{-}o\text{-}C}$ = 739 Hz), 132.66 and 133.87 ($J_{Tl\text{-}m\text{-}C}$ = 61 Hz), 192.55 and 198.43 (J_{Tl-CO} = 296 Hz), 130.22, 130.73, 135.99, 137.34, 158.11. Anal. Calcd for $C_{17}H_{13}ClF_3O_3Tl$: C, 36.45; H, 2.31. Found: C, 36.55; H, 2.46.

2d: mp 209–213 °C dec (90%); IR (KBr) cm^{-1} 1600–1700 (br); ^1H NMR (DMSO-d_6) δ −2.18 and 8.77 (s, 2 H, CH_2, J_{Tl-CH_2} = 657

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[20] For a discussion of the stability of organomercury, thallium, and lead complexes with anionic and neutral ligands, see: Beletskaya, I. P.; Butin, K. P.; Ryabtsen, A. N.; Reutov, O. A. *J. Organomet. Chem.* **1973**, *59*, 1.

[21] House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, D. *J. Org. Chem.* **1969**, *34*, 2324.

[22] Bell, H. C.; Kalman, J. R.; Pinhey, J. T.; Sternhell, S. *Tetrahedron Lett.* **1974**, 3391.

[23] (a) *CRC Handbook of Data on Organic Compounds*; Weast, R. C., Astle, M. J., Eds.; CRC Press: Boca Raton, FL, 1985; Vol. I, p 413. (b) IR ($CHCl_3$) cm^{-1} 3460 (OH stretching), 1680 (C=O); NMR ($CDCl_3$) δ 1.21 (d, 3 H, CH_3, *J* = 15 Hz), 3.03 (m, 3 H, CH_2 and OH), 3.83 (s, 3 H, OCH_3), 4.45 (m, 1 H, CH), 6.9 and 7.91 (dd, 4 H, aromatic protons); MS, M^+ 194. (c) Kuroda, C.; Matsukuma, T. *Sci. Papers Inst. Phys. Chem. Res. (Jpn.)* **1932**, *18*, 51. (d) Watson, J. M.; Irvine, J. L.; Roberts, R. M. *J. Am. Chem. Soc.* **1973**, *95*, 3348. (e) Kanthi, R. B.; Nargund, K. S. *J. Karnatak Univ.* **1957**; *Chem. Abstr.* **1959**, *53*, 8067d; 2, 8. (f) Vorländer, B. D.; Knötzsch, A. *Ann.* **1897**, *294*, 317. (g) Sukh Dev, *J. Ind. Chem. Soc.* **1956**, *33*, 703. (h) Rohrmann, E.; Jones, R. G.; Shonle, H. A. *J. Am. Chem. Soc.* **1944**, *66*, 1856.

[24] Synthesis of α-acetoxy ketones from trimethylsilyl enol ethers with $Pb(OAc)_4$ has been known in the literature (Rubottom, G. M.; Gruber, J. M.; Kincaid, K. *Synth. Commun.* **1976**, *6*, 59).

Table IV. α-Alkoxylation of α-Metallo Ketone with Iodosobenzene and Alcohols (M = Tl^{III}, Pb^{IV}, and Hg^{II})

α-metallo ketone $RCOCH_2M(OCOR')$, R′ = CH_3 or CF_3	alcohol	product[a]	yield (%)
2a	CH_3OH	$C_6H_5COCH_2OCH_3$	65
2a	C_2H_5OH	$C_6H_5COCH_2OC_2H_5$	70
2c	CH_3OH	*p*-$ClC_6H_4COCH_2OCH_3$	67
2d	CH_3OH	2-pyridinyl-$COCH_2OCH_3$	72
2e	CH_3OH	2-thienyl=$COCH_2OCH_3$	83
3	CH_3OH	*p*-$CH_3OC_6H_4COCH_2OCH_3$	80
4	CH_3OH	*p*-$CH_3OC_6H_4COCH_2OCH_3$	90

[a] All the α-methoxy ketones were characterized by their IR, NMR, and mass spectra and were compared with the literature spectra (Moriarty, R. M.; Prakash, O.; Duncan, M. P.; Vaid, R. K.; Musallam, H. A. *J. Org. Chem.* **1987**, *52*, 150).

Hz), 2.18 and 2.63 (s, 3 H, CH_3, J_{Tl-CH_3} = 27 Hz), 3.25 and 11.99 (m, 2 H, J_{Tl-o-H} = 524 Hz), 6.08 and 8.65 (m, 2 H, J_{Tl-m-H} = 154 Hz), 7.52–8.40 (m, 4 H, aromatic protons). Anal. Calcd for $C_{16}H_{13}F_3NO_3Tl$: C, 36.35; H, 2.46. Found: C, 37.55; H, 2.69.

2e: mp 236–245 °C (94%); IR (KBr) cm^{-1} 1600–1700 (br); ^1H NMR (DMSO-d_6) δ −2.22 and 8.76 (s, 2 H, CH_2, J_{Tl-CH_2} = 659 Hz), 2.06 and 2.60 (s, 3 H, CH_3, J_{Tl-CH_3} = 34 Hz), 3.25 and 11.85 (m, 2 H, J_{Tl-o-H} = 516 Hz), 5.91 and 8.55 (m, 2 H, J_{Tl-m-H} = 158 Hz), 7.15–8.45 (m, 3 H, aromatic protons). Anal. Calcd for $C_{15}H_{12}F_3O_3Tl$: C, 33.77; H, 2.25. Found: C, 33.55; H, 2.25.

2f: mp 274–276 °C (90%); IR (KBr) cm^{-1} 1600–1700 (br); ^1H NMR (DMSO-d_6) δ −2.62 and 8.45 (s, 2 H, CH_2, J_{Tl-CH_2} = 664 Hz), 1.20 (d, 9 H, *t*-$C(CH_3)_3$), 2.13 and 2.63 (s, 3 H, CH_3, J_{Tl-CH_3} = 30 Hz), 3.43 and 11.67 (m, 2 H, J_{Tl-o-H} = 494 Hz), 6.00 and 8.52 (m, 2 H, J_{Tl-m-H} = 151 Hz). Anal. Calcd for $C_{15}H_{18}F_3O_3Tl$: C, 35.47; H, 3.55. Found: C, 35.34; H, 3.60.

(*p*-Methoxyphenacyl)(*p*-methoxyphenyl)lead Diacetate (3). (*p*-Methoxyphenyl)lead triacetate (4.91 g, 10 mmol) was added to the trimethylsilyl enol ether of *p*-methoxyacetophenone (3.33 g, 15 mmol) in dry benzene (20 mL) and the mixture was shaken until all the solid has dissolved. The clear solution was stirred at room temperature overnight. The precipitated solid was filtered, washed with benzene to give **3**, 4.16 g (72%). ^1H NMR ($CDCl_3$) δ 1.87 (s, 6 H, $OCOCH_3$'s), 3.77 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 4.37 (s, 2 H, CH_2), 6.87–8.1 (m, 8 H, aromatic protons). Compound **3** had mp 134 °C. Compound **3** is reported to decompose at room temperature.[12] This discrepancy may be due to the presence of (*p*-methoxyphenyl)lead triacetate in compound **3**. In our hands a purified sample was very stable at room temperature.

Bis(*p*-methoxyphenacyl)mercury (4). Phenylmercury acetate (3.36 g, 10 mmol) was added to the trimethylsilyl enol ether of *p*-methoxyacetophenenone (4.45 g, 20 mmol) in dry benzene (25 mL) and the reaction mixture was stirred at room temperature overnight. The solid thus formed was filtered, washed with benzene, and crystallized from methanol to give **4**, 2.6 g (80%): mp 185–189 °C; IR (KBr) cm^{-1} 1630 (C=O); ^1H NMR ($CDCl_3$) δ 2.98 (s, 4 H, CH_2's), 3.9 (s, 6 H, OCH_3's), 6.93 and 7.96 (dd, 8 H, aromatic protons). Anal. Calcd for $C_{18}H_{18}HgO_2$: C, 43.32; H, 3.61. Found: C, 43.08; H, 3.56.

$C_6H_5COCD_2Tl$(*p*-tolyl)$OCOCF_3$. Deuterioacetophenone was obtained by refluxing a solution of acetophenone in $D_2O/CH_3OD/CH_3ONa$ overnight. Deuterio-**2a** was obtained by the reaction of *p*-tolylthallium(III) bis(trifluoroacetate) and $C_6H_5C(OSiMe_3){=}CD_2$ as described above. The ^1H NMR spectrum of $C_6H_5COCD_2Tl$(*p*-tolyl)$OCOCF_3$ show the absence of peaks at δ −3.27 and 9.62 which appear in the spectrum of **2a** for -$COCH_2Tl$-.

Protonolysis of α-Metalated Ketone. Trifluoroacetic acid (5 mL) was added to the α-metalated ketones (1.0 mmol), and the reaction mixture was stirred at room temperature for 1 h, then poured into water (20 mL), and extracted with ether (3 × 20 mL). The combined ether extracts were washed with aqueous sodium bicarbonate solution and then with water, dried (anhydrous $MgSO_4$), and filtered. Evaporation of the ether layer in vacuo afforded acetophenones (Table I).

Aldol Condensations of α-Metalated Ketones with 1 Equiv of $TiCl_4$. A solution of the α-metalated ketone (1.0 mmol) in dry THF (15 mL) was added dropwise to a solution of the aldehyde or ketone (1.0 mmol) and titanium tetrachloride (1.0 mmol) in dry THF (15 mL) under a nitrogen atmosphere at −78 °C. The reaction mixture was stirred at −78 °C for 1.5 h and at room temperature for 1 h. After addition of water (15 mL), the mixture was stirred at room temperature for another 0.5 h. The reaction mixture was extracted with ether (3 × 20 mL), washed with water, and dried over anhydrous magnesium sulfate. Then the solution was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using first CH_2Cl_2 and then either ether or $CHCl_3$ as an eluant as indicated in Table II.

Lead Tetraacetate Oxidation of α-Metalated Ketones. The α-metalated ketone (1.0 mmol) was added in one portion to a solution of $Pb(OAc)_4$ (1.0 mmol) in acetic acid (10 mL). The reaction mixture was stirred at room temperature for 1–2 h, then poured into aqueous sodium bicarbonate (20 mL), extracted with ether (3 × 20 mL), washed with water, dried (anhydrous $MgSO_4$), and filtered. The residue obtained after concentration of the ether layer was chromatographed on silica gel using CH_2Cl_2/hexane (1:1) as an eluant to yield the pure α-acetoxy ketones (Table III).

Iodosylbenzene Oxidation of α-Metalated Ketones. $BF_3{\cdot}Et_2O$ (1.2 mmol) was added dropwise to a stirred suspension of α-metalated ketone (1.0 mmol) and iodosylbenzene (1.2 mmol) in an alcohol (50–100 mL). The solution was stirred for 1–2 h and then poured into an aqueous sodium bicarbonate solution and extracted with ether (3 × 100 mL). The ether extracts were washed with brine and dried (anhydrous $MgSO_4$). Products were isolated by column chromatography (silica gel), hexane/CH_2Cl_2 3:1) (Table IV).

Acknowledgment. We thank the Office of Naval Research for support of this work under N00014-83K-0306.

Registry No. **1a**, 13735-81-4; **1b**, 55991-65-6; **1c**, 58518-76-6; **1d**, 87221-66-7; **1e**, 62889-07-0; **1f**, 17510-46-2; **2a**, 112481-60-4; **2a**-d_2, 112481-64-8; **2b**, 112481-61-5; **2c**, 112481-62-6; **2d**, 112481-65-9; **2e**, 112461-17-3; **2f**, 112481-63-7; **3**, 84840-87-9; **4**, 112504-69-5; *p*-$CH_3C_6H_4Tl(OCOCF_3)_2$, 23586-55-2; *p*-$CH_3OC_6H_4Pb(OAc)_3$, 18649-43-9; PhHgOAc, 62-38-4; *p*-$CH_3OC_6H_4CHO$, 123-11-5; CH_3CHO, 75-07-0; 2,4-$(CH_3O)_2C_6H_3CHO$, 613-45-6; CH_3COCH_3, 67-64-1; $C_6H_5COCH{=}CHC_6H_4OCH_3$-*p*, 959-33-1; *p*-$CH_3OC_6H_4COCH_2CH(OH)CH_3$, 30314-64-8; 2,4-$(CH_3O)_2C_6H_3CH{=}CHCOC_6H_4OCH_3$-*p*, 18493-34-0; *p*-$CH_3OC_6H_4COCH{=}C(CH_3)_2$, 32097-05-5; *p*-$ClC_6H_4COCH{=}CHC_6H_4OCH_3$-*p*, 6552-63-2; $(CH_3)_3CCOCH{=}CHC_6H_4OCH_3$-*p*, 2419-67-2; *p*-$CH_3OC_6H_4COCH{=}CHCH_3$, 1131-79-9; *p*-$CH_3OC_6H_4COCH{=}CHC_6H_4OCH_3$-*p*, 2373-89-9; $Pb(OAc)_4$, 546-67-8; $C_6H_5COCH_2OAc$, 2243-35-8; *p*-$CH_3OC_6H_4COCH_2OAc$, 58518-78-8; *p*-$ClC_6H_4COCH_2OAc$, 39561-82-5; C_6H_5IO, 536-80-1; $C_6H_5COCH_2OCH_3$, 4079-52-1; $C_6H_5COCH_2OC_2H_5$, 14869-39-7; *p*-$ClC_6H_4COCH_2OCH_3$, 30780-45-1; 2-pyridinyl-$COCH_2OCH_3$, 105729-06-4; 2-thienyl-$COCH_2OCH_3$, 105729-09-7; *p*-$CH_3OC_6H_4COCH_2OCH_3$, 21160-26-9.