Fluorination of Alkenes with Lead(IV) Fluorides: Isolation of a Lead-containing Intermediate

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Summary An organic derivative of lead(IV) was obtained from the reaction of $PbF_2(OAc)_2$ and pregnenolone; some of its reactions are described.

ALTHOUGH organic derivatives of lead have been postulated as intermediates in some reactions of lead(IV) with carbon–carbon double bonds, [1–4] such compounds have apparently not yet been isolated. We report here the isolation and reactions of a compound of this type.

Bornstein's reagent,[2] $PbF_2(OAc)_2$, and $Pb(OAc)_4$–HF (1:4) have been shown to have equivalent chemical reactivities, *i.e.*, cholesterol (**1a**) was transformed into fluorocholestenol (**2a**).[3] When the same reaction was performed with pregnenolone (**1b**) after the usual work up (neutralization with Na_2CO_3) compound (**2b**) was isolated.

However, during the reaction, a white precipitate was formed which was shown to have the formula $C_{25}H_{38}F_2O_6Pb$ from combustion data. This formula can be reconciled with a loose complex between pregnenolone and $PbF_2(OAc)_2$ on the one hand, and a covalent compound having structure (**3**) on the other.

Insolubility of the solid in all usual solvents made spectral studies difficult. Attempted dissolution in $CDCl_3$ resulted in a solution exhibiting the n.m.r. spectrum of (**1b**). Reaction with HF–CH_2Cl_2 at -50 °C, or with CF_3CO_2H–CH_2Cl_2 at 0 °C, afforded (**1b**), (**2b**), and (**4**) (see Table). These results could be reconciled with the loose complex. On the other hand the i.r. spectrum (KBr disc)

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exhibits a band at 450 cm^{-1}, characteristic of a C–Pb stretching vibration.‡ The solid reacted with bromine and benzyl bromide to give (**5a**) and (**6**), with iodine and methyl iodide to give (**5b**) and (**6**), and with acetonitrile to give (**6**), with some (**1b**) and (**2b**) (see Table).§

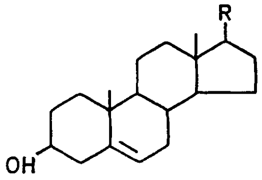
TABLE

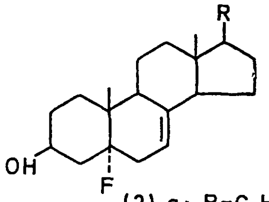
Reaction of compound (**3**)

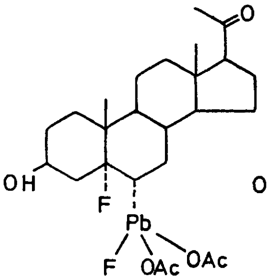
Reagent	Experimental conditions	Products (% yields)
HF–CH_2Cl_2	−50 °C; 2 h	(**1b**) (80); (**2b**) (10); (**4**) 10)
CF_3CO_2H–CH_2Cl_2	0 °C; 1 h	(**1b**) (80); (**2b**) (10); (**4**) (10)
Br_2–CH_2Cl_2	0 °C; 10 min	(**5a**) (95); (**6**) (5)
$PhCH_2Br$–CH_2Cl_2	0 °C; 2 h	(**5a**) (50); (**6**) (50)
I_2–CH_2Cl_2	0 °C, 20 min	(**5b**) (70); (**6**) (30)
CH_3I–CH_2Cl_2	0 °C, 2 h	(**5b**) 50); (**6**) (50)
MeCN	20 °C, 6 h	(**1b**) (35); (**2b**) (5); (**6**) (60)

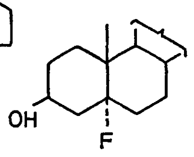
None of these reactions can be reconciled with a loose complex between pregnenolone (**1b**) and $PbF_2(OAc)_2$. It is known that addition of FBr (but not FI) to the 5,6 double bond in a steroid takes place with reverse regioselectivity.[5] Therefore compound (**5a**) cannot have been produced *via* a dissociation of the complex to its constituents. This is especially conspicuous in the case of the reactions of the solid with benzyl bromide and methyl iodide. We feel compelled, therefore, to assign structure (**3**) to the solid, with the lead substituent in the 6α-configuration.

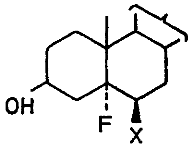
As reactions of tin(IV) derivatives with bromine usually take place with inversion of configuration,[6] the lead substituent can be assumed by analogy to be replaced with inversion and therefore to have the 6α-configuration. This configuration is supported by the rearrangement of compound (**3**) to compound (**6**), as this rearrangement requires an antiperiplanar orientation of the C-10–C-5 and C-6–Pb bonds.[3]

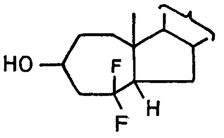

(1) a; R=C_8H_{17}
b; R=COMe

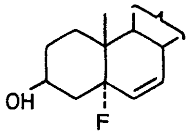

(2) a; R=C_8H_{17}
b; R=COMe


(3)


(4)


(5) a; X=Br
b; X=I


(6)


(7)

Compound (**3**) can apparently readily revert to its constituents, but it can also react by displacement of the lead substituent, either internally [rearrangement to (**6**)] or externally (protolysis by CF_3CO_2H; halogenolysis). Compound (**3**) can also lose HF + $Pb(OAc)_2$ to give compound (**7**) which can be readily isomerized to (**2b**) by the acid formed.

To our knowledge this is the first evidence that some of the reactions of lead(IV) with carbon–carbon double bonds take place in a similar way to reactions with mercury(II)[7] or thallium(III)[8] which are isoelectronic with lead(IV).

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‡ Me_4Pb exhibits a C–Pb stretching vibration at 478 cm^{-1} (E. R. Lippincott and M. C. Tobin, *J. Amer. Chem. Soc.*, 1953, **75**, 4141).

§ All new compounds reported have microanalytical and spectral data in agreement with the proposed structures.

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