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1,3-OXYGEN TO OXYGEN REARRANGEMENTS OF GROUP IV ESTERS

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Abstract: The 1,3-oxygen to oxygen rearrangements of group IV esters of benzoic acid have been studied using ^{18}O isotopic substitution: the free energies of activation for the intramolecular reactions fall from ~190 kJ mol^{-1} for **1A**, to 76 for **1B**, 59 for **1E**, and <52 kJ mol^{-1} for **1F**.

Degenerate rearrangements of silicon from oxygen to oxygen in silyl enol ethers of pentan-2,4-dione, tropolone, and related compounds have been known for some years and may be studied readily by ^{1}H and ^{13}C NMR.[1-7] There are also similar migrations of germyl, stannyl, and carbon centred groups in analogous systems.[3,6,8] Although several related 1,3-shifts of silicon bonded to electronegative elements have also been observed,[9] rearrangement in silyl carboxylic esters have not been reported and indeed can only be observed if oxygen isotopic substituton is used to remove the degeneracy of the rearrangement. We have now detected such rearrangements for esters of Group IV elements from carbon to tin inclusive using ^{13}C and ^{18}O isotopic substitution and ^{13}C NMR and find large changes in activation energies down the Group.


1a **1b**

A: R = CH_2Ph
B: R = $SiMe_3$
C: R = $SiMe_2Bu^t$
D: R = $SiMe_2Bu^s$
E: R = $GeMe_3$
F: R = $SnBu_3$

At ambient temperature trimethylsilyl [^{13}C-carboxyl,$^{18}O_1$]benzoate **1B**[10] shows *two* ^{13}C resonances, separated by 1.69 Hz (at 5.87 Tesla) and exhibiting slight broadening compared with the $^{16}O_2$ isotopomer, corresponding to slow rearrangement. In toluene-d_8 solutions coalescence was observed at 324±2K and this was sensibly constant over a wide range of concentration and solvent polarity (Table). We conclude that the rearrangement is intramolecular *via* a pentacoordinate silcon intermediate or transition state that does not involve significant charge separation. In agreement with this the free energy of activation is slightly *higher* for the more hindered silyl ester **1C** (Table).

Table. Rates of rearrangement **1a**$\rightleftharpoons$**1b** of compounds 1A-1F.[a]

R (solvent)	T_c/K	$\Delta\nu$	k_c (s^{-1})[b]	$\Delta G^{\ddagger}$/kJ mol^{-1}
$SiMe_3$ (toluene)	324±2	1.709±0.002	3.80±0.004	76.0±0.5
(THF)	326±2	1.713±0.008	3.81±0.02	76.5±0.8
(CCl_4)[c]	322±2	1.71±0.01	3.80±0.02	75.5±0.9
(CCl_4)[d]	326±3	1.71±0.01	3.80±0.02	76.0±1.0
$SiMe_2Bu^t$ (toluene)	330±2	1.73±0.01	3.84±0.02	77.4±0.9
$GeMe_3$ (toluene)	253±2	1.46±0.01	3.24±0.02	59.2±0.9
$SnBu_3$ (toluene)	<220	1.2[e]	2.7	<52
$PhCH_2$[f]			10^{-6} (533K)	~190

[a] 0.1 M unless otherwise stated. [b] Ref. 17. [c] 0.13 M. [d] 0.026 M
[e] Estimate [f] Neat samples of **1Aa**, sealed under N_2, with partial decomposition.

The stereochemistry of the rearrangement at silicon was investigated using dimethyl-2-butylsilyl benzoate (**1D**). The diastereotopic methyl groups show two signals in the ^{13}C NMR spectrum at room temperature. Unfortunately estimation of the coalescence temperatures was hampered by a decrease (0.017 Hz/K) in line separation at higher temperatures. There was, however, still a clear separation (0.33 Hz, without significant line broadening) at 350 K, indicating that the silyl shift is occurring with retention of configuration and that inversion must have $\Delta G^{\ddagger} > 87$ kJ mol^{-1}. Retention of configuration at silicon has been observed for enol ethers of pentan-2,4-dione[2,4] and tropolone[4] and is consistent with an internal nucleophilic displacement rather than a [1,3]sigmatropic rearrangement.[12]

The ^{13}C spectra of trimethylgermyl [^{13}C-carboxy, $^{18}O_1$]benzoate **1E**[13] corresponded very closely to those of the silicon analogue **1A** except that the coalescence was at a lower temperature, as expected.[3] The corresponding spectra for the tributyltin ester **1G**[14] showed no decoalescence on cooling before broadening (at 220K), that increased monotonically with decreasing temperature, prevented further useful measurements. In this instance we can set only an upper limit for the activation energy, assuming that the oxygen isotope effect on the ^{13}C chemical shift may be estimated adequately by extrapolation from the values observed for the esters **1A**, **1B**, and **1E**.

Benzyl [^{13}C-*carboxy*, ^{18}O-*ether*]benzoate **1Aa**[11] very slowly rearranges to the ^{18}O-carbonyl isotopomer at 260°C[16]: as yet we have not been able to carry out detailed studies to determine the mechansim so that the first order rate constant (Table) is a *maximum* estimate for an intramolecular 1,3-shift and the activation free energy is a *minimum* value for such a rearrangement. Intramolecular benzyl migration has been observed for the benzyl enol ether of 3-bromotropolone.[6]

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