

926. Aromatic Reactivity. Part XXVIII.¹ The Mechanism of Acid Cleavage of Aryl-Silicon, -Germanium, -Tin, and -Lead Bonds.

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Cleavages of Ar-MR₃ bonds, where M = Si, Ge, Sn, or Pb, by hydrochloric acid in aqueous dioxan have been shown to be significantly slower if deuterium oxide is used in place of protium oxide in the medium. It is concluded that the rate-determining step in each case is the proton transfer from the oxonium ion to the aromatic compound, probably to form an intermediate, [Ar(H)(MR₃)]⁺.

To throw light on the mechanism of acid cleavage of Aryl-MR₃ bonds, where M = Si, Ge, Sn, and Pb,^{2,3} we have measured the solvent isotope effect in several such reactions. The medium was dioxan containing hydrogen chloride and approximately 25 mole-% of protium oxide or deuterium oxide at 50.0°; results are in Table I.

TABLE I.

Cleavage of *p*-X·C₆H₄·MR₃ compounds at 50.0° in dioxan containing hydrogen chloride and approximately 25 mole-% water.

R ₃ M	X	[HCl] * (M)	10 ³ k _{H₂O} (min. ⁻¹)	10 ³ k _{D₂O} (min. ⁻¹)	k _{H₂O} /k _{D₂O}
Me ₃ Si	OMe	4.71	38.5	24.8	1.55
Et ₃ Ge	OMe	4.35	140	82	1.71
		3.23	58.9	34.5	1.71
		3.18	57.5	33.0	1.74
		2.36	30.9	17.6	1.76
		1.80	17.7	10.1	1.75
Et ₃ Ge	CH ₂ SiMe ₃	4.71	29.6	18.5	1.60
Et ₃ Sn	H	0.903	156	63.6	2.45
		0.507	39.6	15.0	2.64
Et ₃ Pb	H	0.00304	35.1	11.5	3.05

* Concentration of a solution of hydrogen chloride in dioxan, 1 ml. of which was added to 1 ml. of dioxan and 1.2706 g. of protium oxide or 1.4123 g. of deuterium oxide.

The most important feature of the results is that there is a positive solvent isotope effect which in all cases is large enough to be used as a criterion of mechanism.⁴ The smallest k_{H₂O}:k_{D₂O} ratio measured is that for *p*-methoxyphenyltrimethylsilane, *viz.*, 1.55 at 50° (which is equivalent to a slightly larger ratio at 25°), and this represents a minimum value since the use of protium chloride reduced the effective isotopic purity of the deuterium oxide to about 97%. Such dilution of the deuterium was much less important in the cleavage of the tin and lead compounds since less acid was required, and this must account for some of the increase in the k_{H₂O}:k_{D₂O} ratio which occurs as the metal is changed in the sequence Si, Ge, Sn, and Pb, but only, we believe, for a little of it.

The magnitude of the solvent isotope effects are such that it seems safe to conclude that a proton transfer from medium to substrate is involved in the rate-determining step.⁴ The simplest mechanism consistent with this, and with a body of other information about these cleavages, is that shown in equation (1), with step (i), formation of the intermediate (I), rate-determining. (The product R₃M·O⁺H₂ would be unstable, and might have no independent existence.)

The size of the k_{H₂O}:k_{D₂O} ratio approaches the theoretical maximum in the case of the tin and lead compounds,⁴ which means that the O-H bond of the oxonium ion is broken

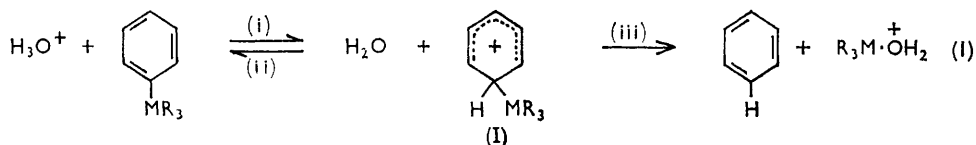
¹ Part XXVII, Baker, Bott, Eaborn, and Greasley, *J.*, 1964, 627.

² Eaborn, *J.*, 1953, 3148; 1956, 4858; Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353; Benkeser, Hickner, Hoke, and Thomas, *ibid.*, 1958, **80**, 5289; Deans and Eaborn, *J.*, 1959, 2299; Eaborn and Moore, *J.*, 1959, 3640; Eaborn and Pande, *J.*, 1961, 297, 3715, 5082; Eaborn and Waters, *J.*, 1961, 542.

³ Eaborn and Pande, *J.*, 1960, 1566.

⁴ Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 3207, 3214.

in the transition state of step (i) to about the same extent as the C-H bond is formed. With the less reactive aryl-silicon and -germanium compounds, however, the transition state of step (i) must be closer to the intermediate (I) in structure, so that the forming



C-H bond is stronger and this compensates for the breaking of the O-H bond and leads to a smaller solvent isotope effect.

The new results do not rule out the possibility of a four-centre process of type (II),³ or of some more complex cyclic process in which the proton electrophil and the oxygen nucleophil come from different solvent molecules associated by hydrogen bonding. The four-centre process is less attractive, however, now it is known that cleavage of an aryl-silicon bond by bromine in carbon tetrachloride, for which a four-centre mechanism would be much more likely than in acid cleavage, proceeds with inversion of configuration at the silicon atom.⁵ The process (II) was proposed originally³ because the reactivity sequence for the Aryl-MR₃ compounds, namely M = C ≪ Si < Ge ≪ Sn ≪ Pb, could not be explained in terms of an intermediate (I), since available electronegativity values^{3,6} indicated that electron release towards carbon (and thus a stabilization of the intermediate (I), with consequent increase in reactivity) increased in order H < R₃C < R₃Pb < R₃Ge < R₃Si ≈ R₃Sn; to explain the observed reactivity sequence it seemed necessary to postulate that breaking of the Aryl-MR₃ bond [the strength of which probably falls in the order M = Si > Ge > Sn > Pb] accompanied proton transfer.³ More recently, however, it has been shown that electron release to a saturated carbon atom increases in the sequence H < Me₃C < Me₃Si < Me₃Ge < Me₃Sn,⁷ and there is no reason to assume that a further increase does not take place to the Me₃Pb group.* The observed reactivity increase from silicon to lead compounds can thus be attributed to increasing stabilization of the intermediate (I).† It is also likely that the importance of p_π-d_π bonding between the aromatic ring and the MR₃ group falls in the sequence Si > Ge > Sn > Pb (cf. ref. 8); if this is so, stabilization of the initial Ar-MR₃ compound by such bonding [which is absent from the intermediate (I)] would also contribute to the increase in rate from M = Si to Ge to Sn to Pb.

It is noteworthy that [*p*-³H₁]trimethylsilylmethylbenzene has recently been shown⁹ to be some 10⁵ times as reactive as [³H₁]benzene in detritiation by trifluoroacetic acid at 25°. If this effect is taken to reflect the stabilization of the intermediate (IV) relative to that of (III), then stabilization by a comparable amount of intermediate (V) relative to (III) could be expected, in agreement with the observation that the Ar-SiMe₃ bond is cleaved some 10⁴ times more readily than the corresponding Ar-T bond in aqueous sulphuric acid at 25°.³ The analogy we postulate is more clearly revealed by the canonical forms (VI) and (VII) of (IV) and (V), respectively; in each case the trimethylsilyl group releases electrons through a saturated carbon atom to stabilize a neighbouring positive charge.

* Prior (rapid) co-ordination of a water molecule to the metal may possibly increase the electron release from the tin and lead atoms.⁹

† On the basis of stabilization of the intermediate (I), the Ar-CMe₃ bond would be expected to be more easily cleaved than the Ar-H bond, contrary to experience; ³ it is likely that step (iii) of equation (1) is rate-determining in the de-t-butylation.

⁵ Eaborn and Steward, *Proc. Chem. Soc.*, 1963, 59.

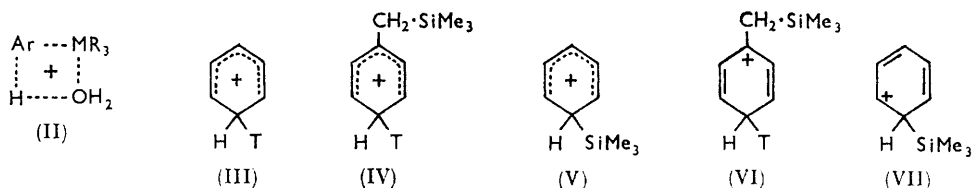
⁶ Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, 5, 269.

⁷ Bott, Eaborn, Pande, and Swaddle, *J.*, 1962, 1217; Bott, Eaborn, and Walton, *J. Organometallic Chem.*, 1964, 2, 154.

⁸ Bedford, Bolton, Carrington, and Prince, *Trans. Faraday Soc.*, 1963, 59, 53; Griffiths and McAfee, *Proc. Chem. Soc.*, 1961, 456.

⁹ Bancroft, Bott, and Eaborn, unpublished results.

We have also measured the solvent isotope effect for cleavage of *p*-chlorophenyltrimethylsilane in trifluoroacetic acid containing 0–32 mole-% of water; the rate passes through a maximum at about 15 mole-%, as the concentration of water is increased, and



over the range of composition reaction is 6–7 times slower in the deuterated medium ($\text{CF}_3\cdot\text{COOD} + \text{D}_2\text{O}$) at 25° , indicating that proton-transfer is again rate-determining. Details will be given in a separate publication.

EXPERIMENTAL

Rate Studies.—For each run, either protium oxide (1.2706 g.) or deuterium oxide (99.8%) (1.4123 g.) was weighed into a stoppered bottle. There were added 1.00 ml. of a solution of the $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{MR}_3$ compound in dioxan at 20° and 1.00 ml. of a solution of protium chloride in dioxan at 20° , the concentration of which is shown in Table 1. (This concentration was determined by titration immediately after some of the stock solution was taken for the reaction medium.) Some of the mixture was transferred to a stoppered quartz absorption cell, and the rate of cleavage was measured spectrophotometrically at 50.0° by the method previously described.^{2,3} The wavelength, λ , used is shown in Table 2.

TABLE 2.

R_3M	Me_3Si	Et_3Ge	Et_3Ge	Et_3Sn	Et_3Pb
X	OMe	OMe	CH_2SiMe_3	H	H
λ (m μ)	284	284	247	259	259

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