Tetrahedron Letters No. 7, pp 595 - 598, 1977. Pergamon Press. Printed in Great Britain.

THE MECHANISM OF ELIMINATION FROM OXYGEN-CONTAINING ORGANOTIN DERIVATIVES. RETROENE AND HOMORETROENE REACTIONS INVOLVING CARBON-METAL BONDS

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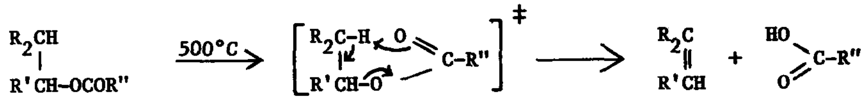
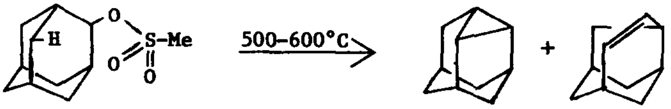
(Received in USA 10 August 1976; received in UK for publication 14 January 1977)

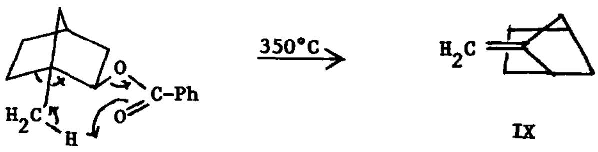
The gas phase pyrolysis of esters and other organic functions with the formation of olefins (retroene reaction) has been known for a long time.[1] The reaction is a concerted 1,2-elimination via a cyclic transition state (Equation 1).[1] Similarly, a number of 1,3-eliminations were reported.[2] Depending upon the structure of the substrate the product was a cyclopropane derivative or an alkene with rearranged skeleton (homo-retroene reaction). For example, 2-adamantyl mesylate (V) formed a mixture of 2,4-dehydroadamantane (VI) and protoadamantene (VII) (Equation 2),[2n] while 1-methyl-2-exo-norbornyl benzoate (VIII) gave 2-methylenenorbornane (IX), exclusively (Equation 3).[2e]



I II III IV (1)



V VI VII (2)

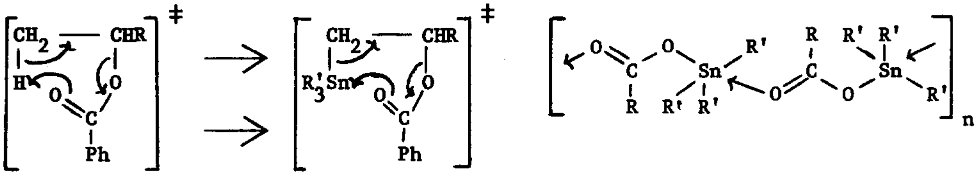


VIII IX (3)

By using isotope labelling in V and studying the regioselectivity in the case of other "cage" polycyclic substrates it was shown that 1,3-eliminations are also concerted reactions.[3] On the other hand, detailed studies of structural factors in reaction (1) have shown that the concertedness of electron movement is imperfect and partial charges develop in the transition state (cf. the direction of arrows in II).[4] Also, a large primary isotope effect was measured when the β-hydrogen eliminated from I was replaced by deuterium.[4d] It can then be predicted that replacement of the hydrogen being eliminated (β-hydrogen or γ-hydrogen, for 1,2 or 1,3-eliminations, respectively) by a more electropositive element, which at the same time is less strongly bonded to carbon, should significantly decrease the activation energy of these reactions. We show here that there are already enough data available to support this assertion for organotin derivatives.

In Chart 1 the energies of bonds broken and formed in the decomposition of a secondary alkyl benzoate (IIa) and its β-trialkyltin derivative (X) are compared. Taken together with the data about the transition state structure discussed above, the comparison substantiates the assertion that concerted elimination is much easier in X than in IIa. Moreover, tin in organotin derivatives tends to increase its coordination number[5] (for instance, organotin carboxylates are represented by formula XI[5b]), a tendency which should also make the elimination easier, since more of the energy of the newly formed bond is liberated in the transition state.

Chart 1



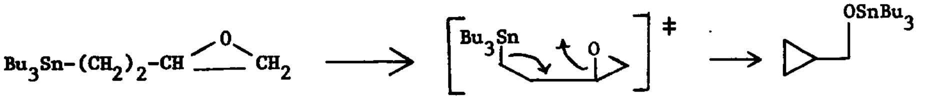
IIa X XI

	IIa	X
Broken:	C-H, 98 Kcal/mol[6]	C-Sn, 47 Kcal/mol[8]
Formed:	O-H, 102 Kcal/mol[7]	O-Sn, 76 Kcal/mol[9]
Difference:	-4 Kcal/mol	-29 Kcal/mol

In fact, reactions in which a tin atom is transferred in a cyclic transition state are rather common.[10] Highly pertinent to this disucssion are: the finding that 1,3-elimination from the mesylate XII in acetic acid does not involve ion pair formation (i.e., solvolysis), but is a concerted elimination,[11] and the cylization of XIII on glc (silicone SE-30, 150°C)[12] for which we propose the cyclic transition state XIV. Another very interesting observation was reported in a study on the synthesis of (2-acetoxyethyl)-triphenyltin (XV).[13] Attempted vacuum distillation at 180°C led to complete decomposition (Equation 6).[13] This represents a dramatic acceleration when compared with the decomposition of ethyl acetate.[1]

(4)

XII, R=H, Me



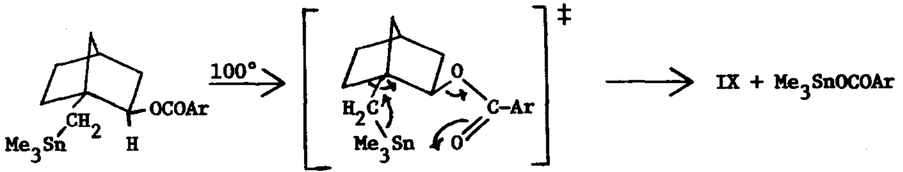
(5)

XIII XIV

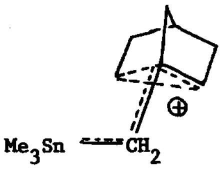
$$Ph_3SnCH_2CH_2OAc \xrightarrow{180°C} CH_2 = CH_2 + Ph_3SnOAc \quad (6)$$

XV

Replacement of acetate in XV by benzoate should lower the activation barrier for Equation 6 even more.[1,4] Also, the elimination should be easier for a secondary ester.[1,4] Thus, based on the comparison of reactions (1) (R=R'=H, R"=Me) and (6) it can be predicted that the reaction analogous to (3) in the organotin series should be reasonably fast at 100°C or below. Indeed, it was found that XVI decomposes smoothly on heating in aqueous acetone, according to Equation (7).[14] The reaction was interpreted as an ionization with the formation of the stabilized ion XVII,[14,15] but a study of the effect of solvent ionizing power upon rate (as it was done for Equation 4) was not undertaken.[14] We propose the cyclic transition state XVIII as a more probable alternative.



XVI XVIII (7)



XVII

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9. This value was calculated for the Sn-OH bond in $Sn(OH)_4$ from ΔH_f for $Sn(OH)_4$: -270.5 Kcal/mol, ("Handbook of Chemistry and Physics", 50th edition, R. C. West, Editor, The Chemical Rubber Co., Cleveland, Ohio, 1969, p. D71) and ΔH_f for HO: +9.3 Kcal/mol (*ibid.*, p. F-164).

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15. For the ionization of XV, a more reasonable interpretation might be the direct formation of a rearranged, non-bridged, ion *via* a bridged transition state.