Journal of Organometallic Chemistry, 82 (1974) C30—C34

Preliminary communication

DEOXYMETALATION REACTIONS. THE CONCERTED NATURE OF 1,3-DEOXYSTANNYLATION

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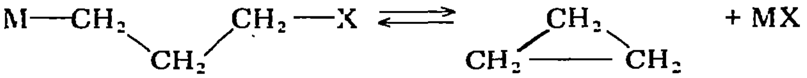
(Received September 19th, 1974)

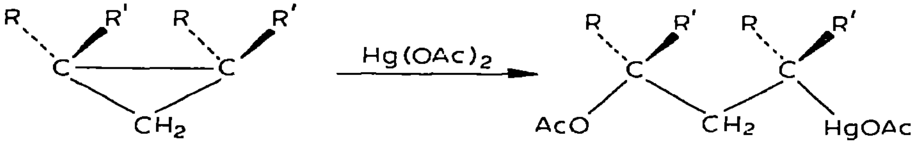
Summary

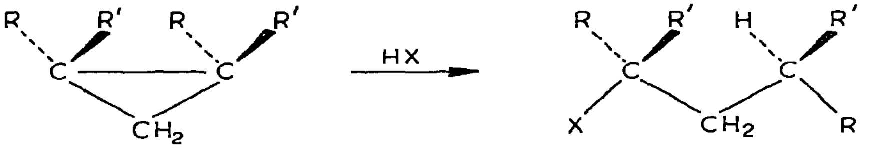
Kinetic and product studies of the solvolysis of γ-R_3M-substituted mesyloxypropanes allow a distinction to be made between a concerted 1,3-elimination and reaction pathways involving metalated cyclopropanes or percaudally-homoconjugated ions.

The formation of cyclopropanes via intramolecular electrophilic aliphatic substitution reactions [1] and their microscopic reverse, the electrophilic cleavage of cyclopropanes [2,3], have been the topic of recent stereochemical studies:

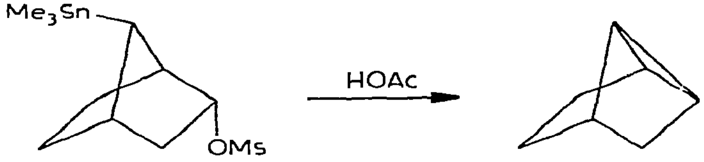


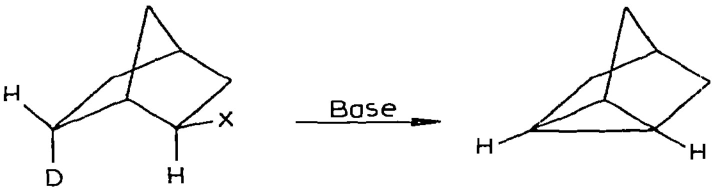
The cleavage of cyclopropanes by electrophile—nucleophile pairs generally occurs with inversion of the carbon undergoing nucleophilic substitution [4] and with stereochemistries which depend upon the nature of the electrophile and substrate at the other carbon. In unhindered systems protonic attack generally leads to retained stereochemistries [3] while mercuric salts give mainly inversion at the carbon undergoing electrophilic attack [2].





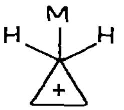
The formal microscopic reverse of the metal—salt cleavage reaction, a 1,3-deoxymetalation reaction, has been shown by us to occur with inversion at both centers [1]. The 1,3-eliminations in which the electrofuge is a proton generally occur with retention [5,6]. Some exceptions to these generalities are known [6].





Corner and edge-metalated cyclopropanes have been suggested as intermediates in the ring-opening reactions [2,3] and by implication then in the ring-forming reactions.

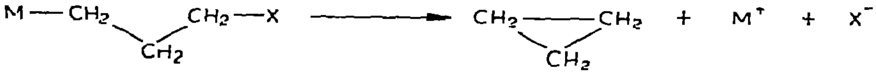
Edge-protonated cyclopropane

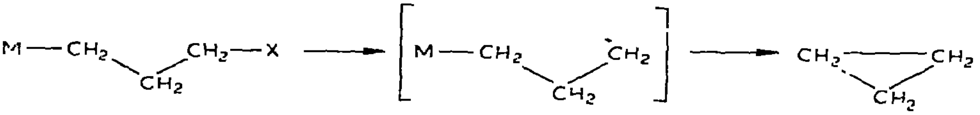


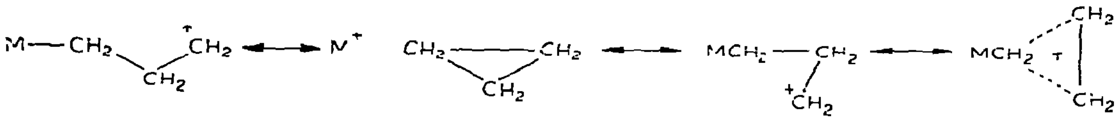
Corner-metalated cyclopropane

We have investigated this proposal by a study of the 1,3-deoxystannylation reaction which is particularly well suited to kinetic studies.

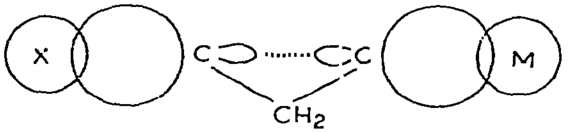
Significant rate accelerations have been observed in the acetolysis of γ-trimethyltin-substituted sulfonates [1,7]. The rate accelerations can be accounted for by either of two reasonable mechanisms; a concerted 1,3-elimination reaction in which the carbon—metal bond supplies internal nucleophilic assistance in an S_N2-like process or a nonconcerted process in which intermediate ions or ion-pairs are formed. The latter carbonium ion may be stabilized by resonance interaction with the carbon—metal bond, i.e. an S_N1-like process leading to a corner- or edge-metalated cyclopropane.







The stereochemical consequence of double inversion [1] limits reasonable structures for intermediates and transition states to those differing little from the W-conformation. Orbital overlap in this arrangement is necessarily



through the back side of the reacting carbons, presumably involving the "tails" of the sp^3 orbitals. This unique arrangement can be described as percaudal homoconjugation and may lead to significant stabilization of an ion. If discrete cationic intermediates are not involved then the percaudal interaction would be a transition state for the 1,3-elimination reaction.

To distinguish between these alternatives we have applied a number of tests to the solvolysis of trimethylmetal-substituted methanesulfonates (mesylates) including: solvent effects, varying the metal and substituents in the electrofugal group, and the effects of α-methyl substitution at the carbon bearing the mesyloxy group.

The rate data shown in Table 1 were obtained conductometrically using acetic acid—water mixtures as solvent.

Mesylates [8] were prepared from the known alcohols [9] and had spectral properties consistent with the proposed structures. Cyclopropane yields were measured manometrically and identity of volatile products confirmed by mass spectrometry.

The effect of ionizing power of the solvent on the rates was analyzed in terms of a Winstein—Grunwald plot using mixtures of aqueous acetic acid. The value of m determined from this data for 3-trimethyltinmesyloxypropane is 0.35.

TABLE 1

RATE DATA FOR SOLVOLYSIS OF R_3M-SUBSTITUTED MESYLOXYPROPANES IN HOAc[a]

Compound	T(°C)	$k_2 \times 10^5$ sec	k_{rel}	Cyclopropane products (%)[b]
$CH_3CH_2CH_2OMs$	100	1.04		0
	75	0.097	1.0	
$Me_3SnCH_2CH_2CH_2OMs$	50	21.2		> 95
	75	138	1425	
	100	(750)[c]		
$Me_3SiCH_2CH_2CH_2OMs$	75	1.42	14	57
	100	12.4		
$Pb_3SnCH_2CH_2CH_2OMs$	100	20.5	20	> 95
$CH_3CH_2CH(CH_3)OMs$	50	0.857	(1.0)	0
	75	11.5		
$Me_3SnCH_2CH_2CH(CH_3)OMs$	50	733	(855)	> 95
	25	60		
$Me_3SiCH_2CH_2CH(CH_3)OMs$	50	6.72	(7.8)	0
	75	101		
	100	753		

[a]Containing 0.5 M H_2O. [b]Non-volatile products include R_3M-substituted propyl- and butyl-acetates. Me_3SnOAc and $(Me_3Si)_2O$ are the major organometallic products. [c]Extrapolated.

TABLE 2

EFFECT OF IONIZING POWER ON SOLVOLYSIS RATE FOR 3-TRIMETHYLTINMESYLOXYPROPANE IN AQUEOUS ACETIC ACID AT 50°

$[H_2O]$	Y[a]	$k_t \times 10^5$ sec
0.45	−1.42	19.2
0.50	−1.38	21.2
0.95	−1.17	22.7
2.45	−0.70	34.2
4.45	−0.34	44.5

[a]Y-values interpolated from the data of A.H. Fainberg and S. Winstein, J. Amer. Chem. Soc., 78 (1956) 2770 ($\log k_t = \log k_0 + mY$).

S_N2 reactions generally exhibit m-values in the range of 0.25-0.35 while S_N1 processes show much higher values near unity [10]. If this reaction were proceeding through an assisted-pathway to ions or ion pairs then the observed rate constant would be equal to $f(k_\Delta)$ since the product is solely cyclopropane [11]. It is a fact that $f(k_\Delta)$-terms are very sensitive to solvent ionizing ability and this property has been extensively employed in solvolytic mechanism studies [12].

The α-Me-effect, k(s-Bu)/k(n-Pr), in the parent system is 118 (75°). The corresponding ratios for the trimethyltin- and trimethylsilyl-substituted mesylates are 35 (50°) and 71 (75°). Since the silicon system is proceeding with only 57% elimination, the α-Me-effect is consistent with a ratio intermediate between that for elimination and substitution reactions. These low ratios imply that no large degree of positive charge is being generated at the carbon bearing the nucleofuge [13].

More striking differences in reactivity occur when the electrofugal groups are altered. Comparison of the rates for the assisted pathways shows the trimethyltin compounds to be 200 times more reactive than the comparable silyl compounds. When the methyl groups on tin are replaced by phenyl groups a 50-fold rate decrease is observed.

The implications of a concerted elimination in the 1,3-deoxystannylation reaction relative to the cleavage of cyclopropanes are not entirely clear but provide no evidence through microscopic reversibility arguments that metalated or percaudally stabilized ions are necessary intermediates in this closely related reaction.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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