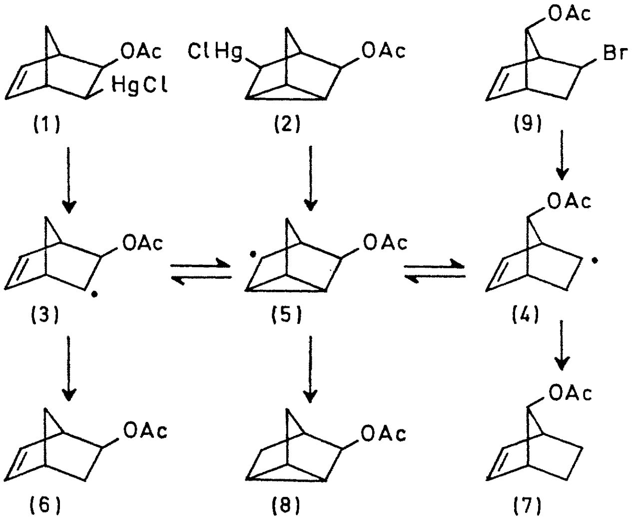
Rearrangements of Norbornenyl Radicals: Further Evidence as to the Mechanism of Borohydride Reduction of Organomercurials

By V. M. A. Chambers, W. R. Jackson,* and (in part) G. W. Young

(*Department of Chemistry, Queen's University, Belfast* BT9 5AG, *Northern Ireland*)

Summary Reductions of 3-acetoxy-5-norbornen-2-yl mercuric chloride, 5-acetoxy-3-nortricyclyl mercuric chloride, and 7-*anti*-acetoxy-2-*exo*-bromonorborn-5-ene with tributyltin hydride, triphenyltin hydride, or photochemically in methanol give similar isomeric mixtures of 2-*exo*-acetoxynorbornene, 7-*anti*-acetoxynorbornene, and 3-acetoxynortricyclene, as does reduction of the mercurials with sodium borohydride in aqueous tetrahydrofuran, indicating that a radical mechanism operates in the latter reaction.

In a recent communication[1] concerned with the sodium borohydride reduction of 3-acetoxy-5-norbornen-2-yl mercuric chloride (**1**) and 5-acetoxy-3-nortricyclyl mercuric chloride (**2**), it was suggested that an interconverting mixture of three radicals (**3**), (**4**), and (**5**) was produced, leading to the formation of a mixture of 2-*exo*-acetoxynorborn-5-ene (**6**), 7-*anti*-acetoxynorborn-2-ene (**7**), and 3-acetoxynortricyclene (**8**). We have now studied the reduction of (**1**) and (**2**) with tri-n-butyl- and triphenyl-tin hydride and deuteride. High yields of the acetates were obtained and the product ratios are given in Table 1. These ratios are seen to be very close to the values obtained from reductions of (**1**) and (**2**) with sodium borohydride. As the tin hydrides normally function as free-radical reducing agents,[2] these results give further support to a radical mechanism in the borohydride reduction. Additionally, reduction was inhibited by addition of a small sample of hydroquinone. When the product from a reduction with tri-n-butyltin deuteride was separated by preparative g.l.p.c., samples of (**7**) and (**8**) were obtained whose n.m.r. spectra (100 MHz) were identical with those of the deuteriated acetates from sodium borodeuteride reduction, indicating that the stereochemistry of reduction was similar in the two reactions. Similar results and conclusions have recently been obtained by Whitesides and Filippo.[3]



The above results could be explained by oxidation of the initially formed radicals to carbonium ions and their subsequent rearrangement. However, when (**1**) and (**2**) were reduced by photolysis in methanol solution† the acetates were again obtained in high yield in ratio very similar to that from the borohydride reduction. No methoxy-acetates were detected, indicating that carbonium ions were not involved.

TABLE

Reduction of 3-acetoxy-5-norbornen-2-yl mercuric chloride (**1**) *and 5-acetoxy-3-nortricyclyl mercuric chloride* (**2**) *at 20°*

Compound	Reductant	Solvent	Time	Yield (%)	Product composition (**6**)	(**7**)	(**8**)
(**1**)	$NaBH_4$	Aqueous THF			6	34	60
(**2**)	$NaBH_4$	Aqueous THF			6	34	60
(**1**)	$Bu^n{}_3SnH$[a]	neat	2 h	90	12	35	53
(**2**)	$Bu^n{}_3SnH$[a]	neat	2 h	85	8	35	57
(**1**)	Ph_3SnH[a]	neat	1 h	90	14	32	54
(**2**)	Ph_3SnH[a]	neat	1 h	90	8	31	61
(**1**)	*h*ν	MeOH	5 days	85	5	27	68
(**2**)	*h*ν	MeOH	5 days	85	5	27	68

quimolar quantity.

The reduction of 7-*anti*-acetoxy-2-*exo*-bromonorborn-5-ene (**9**)[4] with tin hydrides was also investigated in homogeneous solutions. For reductions with triphenyltin hydride in benzene solution a concentration-dependance of product ratio was observed. In concentrated hydride solutions the proportion of (**7**) formed by hydrogen atom transfer to the initially formed radical (**4**) increased considerably, as shown in Table 2. Use of the previously assessed values of the rate constant for hydrogen atom transfer from triphenyltin hydride to cyclohexyl radicals[5] and the assumption that (**4**) ⇌ (**5**) ⇌ (**3**), but that (**4**) does not interconvert directly with (**3**), gives a value of *ca.* $4 \times 10^7\ s^{-1}$ for the unimolecular rate constant for the isomerisation of (**4**). Reductions with the slower hydrogen atom transfer reagent, tri-n-butyltin hydride,[5] showed no appreciable concentration-dependance. It is not possible from our limited data to speculate whether any of the nortricyclyl acetate (**3**) arises by concerted cyclisation of (**4**) as has been suggested for the formation of methylcyclopentane from the 5-hexenyl radical.[6]

TABLE 2

Reductions of 7-anti-*acetoxy*-2-exo-*bromonorborn-5-ene* (**9**)

Reductant	[Hydride]	Temp.	Time	Product composition (**6**)	(**7**)	(**8**)
$Bu_3{}^nSnH$	*ca.* 4 mol. (neat)	25°	24 h	8	35	57[a]
Ph_3SnH	*ca.* 4 mol. (neat)	25°	12 h	8	49	43[a]
Ph_3SnH	0·45 M[b]	38·5° ±0·2°	3·5 days	9	41	50
Ph_3SnH	0·36 M[b]	38·5°	3·5 days	8	39	53
Ph_3SnH	0·16 M[b]	38·5°	3·5 days	8	36	56
Ph_3SnH	0·12 M[b]	38·5°	3·5 days	8	35	57

[a] The acetates were isolated in 80—85% yield in these experiments.

[b] In these kinetic experiments [halide] = 0·436 M in benzene solution.

Our results clearly establish that the radicals (**3**), (**4**), and (**5**) are in equilibrium. Although the ready conversion of radicals of type (**3**) into type (**5**) has been demonstrated previously, *e.g.* where OAc is replaced by SAc,[7] products derived from radicals of type (**4**) have been observed less frequently. Radical additions to some polychloronorbornadienes have led to 7-substituted products, but the rearrangement in these cases is encouraged by the formation of an α-chloro-radical $>\dot{C}Cl$ in preference to a radical bearing α-hydrogen.[8] Similarly, rearrangements observed in radical additions to hexamethylnorbornadiene involve the formation of a more highly substituted radical.[9] The radical addition of chlorine to benznorbornadiene also gives some 7-substituted product[10] and recently the formation of 7-substituted compounds has been observed in the photochemical addition of cyclohex-2-enone to norbornadiene[11] and in the addition of trimethyltin hydride to norbornadiene.[3] We are investigating reactions involving other substituted norbornenyl and nortricyclyl radicals in an attempt to establish whether similar equilibria exist and if so, how the position of equilibrium varies with substituent.

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† (**1**) (4 g) in methanol (500 ml) was irradiated for 5 days at ambient temperature in a quartz reactor with a low-pressure Hg lamp emitting at 254 and 184 nm.

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[2] H. G. Kuivila, *Accounts Chem. Res.*, 1968, **1**, 299.

[3] G. M. Whitesides and J. S. Filippo, personal communication.

[4] Prepared as described by S. Winstein and M. Shatavsky, *J. Amer. Chem. Soc.*, 1956, **78**, 592. In view of the hazards associated with these experiments (see S. Winstein, *ibid.*, 1961, **83**, 1516) all necessary precautions were taken to avoid exposure to the chemicals involved.

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