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## The Stereochemistry of Organometallic Compounds. Part X.<sup>1</sup> Further Evidence as to the Mechanism of Borohydride Reduction of Organomercurials from a Study of Photochemical and Organotin Hydride Reductions <sup>2</sup>

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Reductions of 3-exo-acetoxynorborn-5-en-2-exo-ylmercury(II) chloride (1), 5-exo-acetoxy-3-exo-nortricyclylmercury(II) chloride (2), 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-acetoxynorborn-5-ene (3), 7-anti-acetoxynorborn-2-ene (4), and 3-acetoxynortricyclene (5) as do reductions of the mercurials with sodium borohydride in aqueous tetrahydrofuran. Reductions of 3-acetoxynorborn-5-en-2-ylmercury(II) chloride and 7-anti-acetoxy-2-exo-bromonorbornene with tributyltin deuteride gives deuterio-substituted acetates, (3), (4), and (5), and the stereochemistry of deuterium incorporation is identical with that obtained by reduction of the mercurials with sodium borodeuteride. The results indicate that a radical mechanism is operating in the reduction of organomercurials with borohydride.

THE reductions of 3-exo-acetoxynorborn-5-en-2-ylmercury(II) chloride (1) and 5-exo-acetoxy-3-exo-nortricyclylmercury(II) chloride (2) with sodium borohydride in aqueous tetrahydrofuran have been shown to give a mixture of 2-exo-acetoxynorborn-5-ene (3), 7-antiacetoxynorborn-2-ene (4) and 3-acetoxynortricyclene (5).<sup>1</sup> The product ratios were discussed as arising from

<sup>1</sup> Part IX, G. A. Gray, W. R. Jackson, and V. M. A. Chambers, *J. Chem. Soc.* (C), 1971, 200.

an equilibrating mixture of the three radicals (6), (7), and (8). In an attempt to demonstrate that radicals were involved as intermediates in these reactions, we have now investigated the reduction of the organomercury halides (1) and (2) with tributyl- and triphenyltin hydrides. The product ratios, determined by analytical g.l.c., were very similar for demercurations

<sup>2</sup> Preliminary communication, V. M. A. Chambers, W. R. Jackson, and G. W. Young, Chem. Comm., 1970, 1275.

with all three reagents and were insensitive to changes in temperature and solvent (see Table 1). Organotin hydrides are known to reduce alkyl halides by a freeradical chain mechanism,3 and the results thus provide



good evidence for the intervention of the radicals (6), (7), and (8) in the borohydride reductions of the mercurials (1) and (2). In addition the reaction of tributyltin hydride with the organomercurial (1) was severely

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acetoxynorborn-2-ene (4), and the deuteriated 3-acetoxynortricyclene (5) showed that the stereochemistry of deuterium incorporation was similar to that found in the borodeuteride reductions of the organomercurials (1)and (2); the spectra were virtually identical with those obtained previously.1 Sufficient quantities of the deuteriated 2-exo-acetoxynorborn-5-ene were also isolated for an n.m.r. investigation. The deuterioacetate was converted into the corresponding 2-exo-alcohol for ease of comparison with published spectra. The alcohol now had a spectrum which integrated for two protons in the region  $\tau$  8.1—8.4, where the 3-exo- and the two 7-protons normally absorb.<sup>4</sup> In addition the multiplet centred at  $\tau$  8.60, which has been assigned to the 3-endoproton, was now greatly simplified but still integrated for one proton. The spectra thus suggest that deuterium has been incorporated almost exclusively into the 2-exoposition. In addition to providing another basis of comparability between reductions with borohydride and tin hydrides, the stereochemistry of deuterium incorporation is consistent with the known stereochemistry of chain termination in related compounds. The stereoselective preference for exo-chain termination in norbornenvl radicals and the non-stereoselective termination in nortricyclyl radicals has been exemplified previously.5,6

The results strongly suggest that a radical mechanism is operating in the borohydride reduction of organomercurials and that the acetoxynorbornenyl and

TABLE 1

Reductions of 3-exo-acetoxynorborn-5-en-2-exo-ylmercury(II) chloride (1) and 5-exo-acetoxy-3-exo-nortricyclylmercury(II) chloride (2)

			hydride]	Temp		Product composition *		
Compound	Reductant	Solvent	[mercurial]	$(T/^{\circ}C)$	Yield (%)	(3)	(4)	(5)
$\overline{(1)}$	NaBH₄	Aq. THF ‡		20		6	34	60 †
(2)	$NaBH_{4}$	Aq. THF		<b>20</b>		6	<b>34</b>	60 †
(1)	Bu₃SnĤ	Neat	1	<b>20</b>	90	12	35	53
(1)	$Bu_3SnH$	Neat	4	<b>20</b>	90	11	31	<b>58</b>
(1)	$Bu_3SnD$	Neat	1	<b>20</b>	90	12	<b>37</b>	51
(1)	$Bu_3SnH$	Ether	1	-78	30	6	35	59
(2)	Bu <sub>3</sub> SnH	Neat	1	<b>20</b>	85	8	35	57
(1)	$Ph_3SnH$	Neat	1	20	90	14	32	54
(1)	$Ph_{3}SnH$	$\mathbf{Neat}$	1	20	90	8	31	61
		* (±3%). † Re	esults from ref. 1.	t Tetrahydrofuran	•			

retarded when a small amount of hydroquinone was present.

The products of a reduction of the acetoxymercurial (1) with tributyltin deuteride were separated by preparative g.l.c., and their mass spectra confirmed that one deuterium atom had been incorporated per molecule. The n.m.r. spectra (100 MHz) of the deuteriated 7-anti-

<sup>3</sup> H. G. Kuivila, Accounts Chem. Res., 1969, 2, 299; H. G. Kuivila, Adv. Organometallic Chem., 1964, 1, 47.
 <sup>4</sup> J. Passivirta, Suomen Kem., 1965, 38B, 135.
 <sup>5</sup> N. O. Brace, J. Org. Chem., 1962, 27, 3027.
 <sup>6</sup> S. J. Cristol and D. I. Davies, Adv. Free Radical Chem., 1965, 1, 155; P. D. Bartlett, G. N. Fickes, F. C. Haust, and B. Holsson, Account, Chem. Bec. 1970, 9, 177.

R. Helgeson, Accounts Chem. Res., 1970, **3**, 177. <sup>7</sup> For leading references see T. Van Auken and E. J. Rick, *Tetrahedron Letters*, 1968, 2709; S. J. Cristol and R. V. Barbour, J. Amer. Chem. Soc., 1968, 90, 2832.

acetoxynortricyclyl radicals (6), (7), and (8) are in equilibrium. However, as has been discussed previously,<sup>1</sup> although the ready interconversion of radicals of types (6) and (8) has been demonstrated, e.g. where OAc is replaced by SAc,7 products derived from radicals of type (7) have been observed in far fewer instances,<sup>8-11</sup>

<sup>8</sup> C. K. Alden, J. A. Claisse, and D. I. Davies, J. Chem. Soc. (C), 1966, 1540; J. A. Claisse, D. I. Davies, and C. K. Alden,

*ibid.*, p. 1498.
<sup>9</sup> E. N. Prilezhaeva, V. A. Asovskaya, G. U. Stepanyanz, D. Mondeshka, and R. J. Shelchtman, *Tetrahedron Letters*, 1969, 4909.

J. J. McCullough, J. M. Kelly, and P. W. Rasmussen, J. Org. Chem., 1969, 34, 2933.
 O. R. Khan, I. J. Tyminski, F. L. Pelezar, and R. Y. Tien,

unpublished observations quoted by H. G. Kuivila, Accounts Chem. Res., 1969, 2, 299.

and in several of these special circumstances encourage the formation of 7-substituted products. In contrast, the cationic equivalents of (6), (7), and (8) are always in rapid equilibrium. It thus seemed possible that the 7-substituted products arose from rearrangements of norbornenyl cations, produced by oxidation of the intermediate radicals. One of the metals present in the system could have acted as an oxidising agent.

Photochemical reduction of the acetoxymercurials (1) and (2) in methanolic solution was therefore investigated. The acetates (3), (4), and (5) were again formed in good yield (>80%) and in the ratio 5:27:68, respectively, similar to that obtained by hydride reductions of the mercurials. The thermal and photochemical decompositions of dialkyl- or diaryl-mercury compounds in alcoholic solutions have been shown to be homolytic in character <sup>12</sup> and to lead to quantitative vields of hydrocarbon, mercury, and formaldehyde.13 Similarly methylmercury(II) iodide and benzylmercury-(II) iodide have been used as sources of radicals in irradiated solutions.<sup>14</sup> Thus further strong evidence for the intermediacy of radicals in the anhydride reduction of organomercurials is obtained. Oxidation of the firstformed radicals to carbonium ions is not significant as no methoxy-acetates were found in the product.

Finally, reductions of 7-anti-acetoxy-2-exo-bromonorborn-5-ene with tributyl- and triphenyl-tin hydrides were investigated. The three acetates (3), (4), and (5)were again formed, and the product ratios were similar but not identical with those obtained in reductions of the mercurials (1) and (2) with tin hydrides. Reductions with triphenyltin hydride showed a dependence of product ratio on hydride concentration (see Table 2) whereas reductions with tributyltin hydride did not (Table 3). The results in Table 2 firmly discount the

## TABLE 2

Reductions with triphenyltin hydride at  $38.5 \pm 0.2^{\circ}$  of 7-anti-acetoxy-2-exo-bromonorborn-5-ene solutions (0.435M) in benzene

	$\begin{array}{c} \text{Product composition} \\ (\pm 2\%) \end{array}$			
[hydride]/M	(3)	(4)	(5)	
0-45	8	41	50	
0.36	8	39	53	
0.16	8	36	<b>56</b>	
0.12	8	35	57	
Reduction in excess of hydride (ca.	8	49	43	
4 mol. equiv.) at $25^{\circ}$ for 12 h				
Reduction of corresponding chloro-	12	41	47	
acetate in excess of hydride (4				
mol. equiv.) at $25^{\circ}$ for $12 \text{ h}$				

possibility of formation of non-classical norbornenyl radicals, in agreement with previous work on the unsubstituted norbornenyl-nortricyclyl system.<sup>15</sup> The results were further analysed by a method based on the

<sup>12</sup> K. C. Bass, Organometallic Chem. Rev., 1966, 1, 391.

<sup>13</sup> G. A. Razuvaev and Yu A. Ol'dekop, *Doklady Akad. Nauk* S.S.S.R., 1949, **64**, 77.

<sup>14</sup> G. E. Corbett and G. H. Williams, *J. Chem. Soc.*, 1964, 3437; D. H. Hey, D. A. Shingleton, and G. H. Williams, *ibid.*, 1963, 1958.

TABLE 3

Reductions with tributyltin hydride at  $40.0 \pm 0.2^{\circ}$  of 7-anti-acetoxy-2-exo-bromonorborn-5-ene solutions (0.435M) in benzene

Product composition			
	$(\pm 2\%)$		
(3)	(4)	(5)	
8	<b>26</b>	66	
8	27	65	
8	<b>28</b>	<b>64</b>	
9	<b>29</b>	62	
9	29	<b>62</b>	
8	34	57	
	Produ (3) 8 8 8 9 9 8	$\begin{array}{c} {\rm Product\ compt} \\ (\pm 2\%) \\ (3)  (4) \\ 8  26 \\ 8  27 \\ 8  28 \\ 9  29 \\ 9  29 \\ 9  29 \\ 8  34 \end{array}$	

work of Carlsson and Ingold.<sup>16</sup> If the rate of rearrangement of (7) is  $k_r$  and the rate of chain termination by hydrogen-atom abstraction from the tin hydride,  $k_t$ , is the same for all three radicals then equation (1) can be established, provided that the assumption, that the

$$(k_{\rm r}/k_{\rm t})[{\rm hydride}] = \{[(4)]/[(3)] + [(5)]\} + {\rm const.}$$
 (1)

equilibrium  $(7) \rightarrow (8) \rightarrow (6)$  obtains, but that (7) does not equilibrate directly with (6), is tenable. A plot of the relative concentration of (4), *i.e.* of  $\{[(4)]/[(3)] +$ (5)]} versus the concentration of hydride gave a straight line of slope 0.44, indicating that the rate of rearrangement of (7),  $k_r$ , is  $ca. 2 \times 10^{-7} \text{ mol}^{-1} \text{ s}^{-1}$ , with a value of  $5 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$  assumed for  $k_t$ . This value of  $k_t$  is the transfer constant for triphenyltin hydride to a cyclohexyl radical and should be a reasonable approximation (cf. ref. 16). The corresponding chain-transfer constant for tributyltin hydride is known to be ca. one fifth of this value,<sup>16</sup> thus explaining the lack of concentration dependance for reductions with tributyltin hydride. Recent work has shown that some of the methylcyclopentane obtained by reaction of tin hydrides with the hex-5-enyl radical arises from a concerted hydrogen-atom transfer-cyclisation mechanism.<sup>17</sup> Our limited data do not allow us to speculate whether any of the nortricyclyl acetate arises from a similar concerted cyclisation.

A preparative scale reduction with tributyltin deuteride followed by preparative g.l.c. of the resulting acetates gave samples of deuteriated (4) and (5). The n.m.r. spectra of these samples were identical with those obtained by tin deuteride reduction of the norbornenylmercurial (1), indicating that the stereochemistry of deuterium incorporation was the same.

The Mechanism of Metal Hydride Reductions of Oxymercurials.—Our results provide strong evidence for the intervention of free radicals in the metal hydride reductions of organomercurials. However, the detailed mechanism of radical formation and hydrogen atom transfer is not clear. The results in Table 1 coupled with the work of Whitesides and Filippo,<sup>18</sup> who report similar

<sup>15</sup> C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, 1966, **31**, 3381.

<sup>16</sup> D. J. Carlsson and K. U. Ingold, J. Amer. Chem. Soc., 1968, **90**, 7047.

 <sup>17</sup> C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, J. Amer. Chem. Soc., 1966, 88, 5361.
 <sup>18</sup> G. M. Whitesides and J. S. Filippo, J. Amer. Chem. Soc.,

<sup>18</sup> G. M. Whitesides and J. S. Filippo, J. Amer. Chem. Soc., 1970, **92**, 6611. product ratios from reductions of the oxymercurials (1) and (2) with organoaluminium and organocopper hydrides, suggest that the organotin hydrides are not the hydrogen transfer agents. Additionally, although the product ratios from tin hydride reductions of the acetoxychloro- and acetoxybromo-norbornenes (see Tables 2 and 3) are similar to those obtained by reductions of the organomercurials, they are not identical, suggesting that an intermediate hydrogen-atom transfer reagent intervenes in mercurial reductions. Such an intermediate could either be an organomercury(II) hydride, RHgH, or, less probably, mercury(I) hydride HgH (cf. refs. 18 and 19).

## EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Analytical g.l.c. was carried out with a Perkin-Elmer F11 gas chromatograph. Peak areas were measured with a Dupont 310 curve resolver and are accurate to  $\pm 2\%$ . Preparative g.l.c. was carried out with an Aerograph Autoprep as described previously.<sup>1</sup> Mass spectra were determined by G. Jordan with an A.E.I. MS 902 spectrometer. N.m.r. spectra, except where otherwise stated, were recorded by R. Spratt and I. Jack with a Varian HA100 spectrometer for deuteriochloroform solutions with tetramethylsilane as internal standard.

Organotin Hydrides.-The following organotin hydrides were prepared by the method of Kuivila and Beumel: 20 tributyltin hydride, b.p. 73-80° at 0.6 mmHg (lit., 20 68-74° at 0·3 mmHg),  $\nu_{\rm Sn-D}$  (film) 1290 cm<sup>-1</sup>; triphenyltin hydride, b.p. 154—160° at 0·1 mmHg (lit.,<sup>20</sup> 162—168° at 0.5 mmHg). The hydrides were stored under nitrogen and a nitrogen atmosphere was maintained during reactions with these compounds.

Tributyltin Hydride Reduction of 3-Acetoxynorborn-5-en-2ylmercury(II) Chloride (1).—The mercurial (4.40 g) was added in small portions to tributyltin hydride (3.12 g) with constant stirring at ambient temperature and the mixture was then stirred for 1 h. Dichloromethane (20 cm<sup>3</sup>) was added, and the mixture was filtered until clear. The dichloromethane was removed under reduced pressure and a clear gum (4.9 g) was obtained. Analytical g.l.c. as described previously showed that the three acetates: exo-2-acetoxynorborn-5-ene (3), anti-7-acetoxynorborn-2-ene (4), and 3-acetoxynortricyclene (5), were present. Preparative g.l.c. gave pure samples of the individual isomers.

A similar preparative separation was carried out on the products (5.7 g) of a reduction of the mercurial (1) (4.9 g)with tributyltin deuteride (3.76 g).

A series of reductions were carried out under different conditions; the results are summarised in Table 1. In these cases the yields were estimated by the use of an internal standard. Dodecane was added to the reaction mixtures and the yields were estimated by measurement of g.l.c. peak areas. Calibration with authentic samples showed that the detector response to dodecane was 1.54times that of an equimolar amount of any of the acetates.

In another experiment the mercurial (1) (200 mg) was added to a solution of tributyltin hydride (140 mg) and hydroquinone (40 mg) in ether (2 cm<sup>3</sup>) containing dodecane

<sup>19</sup> D. J. Pasto and J. A. Gontarz, J. Amer. Chem. Soc., 1969, 91, 719.

(22 mg). The mixture was stirred at ambient temperature and after 1 h a sample  $(0.5 \text{ cm}^3)$  was removed. G.l.c. analysis showed no acetate formation. After 3 h some acetates (ca. 10%) had been formed.

Reductions with triphenyltin hydride were carried out under similar conditions, as were reductions of 3-acetoxy-5-nortricyclylmercury(II) chloride with the tin hydrides.

Photochemical Reductions of Mercurials (1) and (2).-3-Acetoxynorborn-5-en-2-ylmercury(II) chloride (10.0 g)was dissolved in methanol (1 l) and irradiated at ambient temperature with a Hanovia low-pressure mercury lamp (immersion type) for 5 days. It was necessary to clean deposited mercury from the lamp enclosure from time to time. The mixture was filtered and the product was isolated in dichloromethane. Distillation gave a sample of the mixed acetates (3)—(5) (3.3 g, 85%), b.p. 75—85° at 13 mmHg.

Further photochemical reductions of the mercurials (1) and (2) were carried out on a smaller scale [mercurial (5 g)]in methanol (500 cm<sup>3</sup>)]. The product was not distilled but the product ratio was obtained by g.l.c. analysis and the yield was estimated by addition of dodecane as internal standard.

anti-7-Acetoxy-exo-2-bromonorborn-5-ene.- exo-2-Bromonorbornen-7-anti-ol, m.p. 43-45° (lit.,<sup>21</sup> 48-49°) was prepared as described by Winstein and Shatavsky.<sup>21</sup> The alcohol (5.0 g) was dissolved in pyridine (20 cm<sup>3</sup>) and treated with acetic anhydride (10 cm<sup>3</sup>) for 3 days at 0°. Isolation of the product in ether gave anti-7-acetoxy-exo-3bromonorborn-5-ene (4.0 g, 66%), b.p. 48-52° at 1 mmHg,  $n_{\rm n}{}^{20}$  1·5180,  $\tau$  3·90 (m, 5- and 6-H), 5·46 (s, 7-H), 6·26 (dq, endo-2-H), 6.76 (s, 4-H), 7.14 (m, 4-H), 7.76 (tt, exo-3-H), 7.98–8.05 (m, endo-3-H and OAc) with  $J_{2,3}$  (endo) 7.0 Hz,  $J_{2,3}$  (endo, exo) 3 Hz,  $J_{3,3}$  (endo, exo) 4 Hz (Found: C, 46.6; H, 5.0. C<sub>9</sub>H<sub>11</sub>BrO<sub>2</sub> requires C, 46.8; H, 4.8%).

anti-7-Acetoxy-exo-2-chloronorbornene.---An impure sample of exo-2-chloronorbornen-7-anti-ol was prepared from the dichloro-compound, and a sample (7.7 g) was acetylated with acetic anhydride (10 cm<sup>3</sup>) in pyridine  $(20 \text{ cm}^3)$  for 4 days at 0°. The product was isolated in ether and chromatographed on silica. Distillation gave a sample of anti-7-acetoxy-exo-2-chloronorbornene (2.5 g, 30%), b.p.  $68-70^{\circ}$  at 5 mmHg,  $\tau$  3.86 (m, 5- and 6-H), 5.43 (s, 7-H), 6.16 (qd, endo-2-H), 6.80 (q, 1-H), 7.08 (m, 4-H), 7.94 (m, exo-3-H and OAc), 8.80 (q, endo-3-H),  $J_{2,3}$  (endo) 7.0 Hz,  $J_{2,3}$  (endo, exo) 4 Hz,  $J_{3,3}$  (endo, exo) 13 Hz. G.l.c. analysis showed the presence of a small amount of impurity (ca. 8%) which could not be separated and led to incorrect analyses for this compound.

Reduction of anti-7-Acetoxy-exo-2-bromonorbornene with *Tin Hydrides.*—Equimolar amounts of the bromo-acetate (2.0 g) and tributyltin hydride (2.5 g) were mixed at ambient temperature. After a short initiation period (usually ca. 5 min) the solution became warm and was then left for The product was isolated in dichloromethane. 36 h. Analytical g.l.c. showed that the acetates (3)--(5) were present in the ratio 8:34:58 and preparative g.l.c. gave pure samples of the individual esters.

Variation of Product Composition with Hydride Concentration in Reductions of anti-7-Acetoxy-exo-3-bromonorborn-5-ene.—Appropriate amounts of tributyltin hydride (see

<sup>20</sup> H. G. Kuivila and O. F. Beumel, J. Amer. Chem. Soc., 1961,

83, 1246. <sup>21</sup> S. Winstein and M. Shatavsky, J. Amer. Chem. Soc., 1956,

Table 3) or triphenyltin hydride (see Table 2) were placed in each of five 1 cm<sup>3</sup> test tubes, containing azobisisobutyronitrile (0.8 mg). The tubes were flushed with nitrogen, stoppered, and allowed to equilibrate in a thermostatted oil bath. Samples (1.0 cm<sup>3</sup>) of a solution (0.436M) of the acetoxy-bromide in benzene were added and the tubes were again flushed with nitrogen, stoppered, and kept in the thermostatted oil bath for 3.5 days. Product ratios were determined by g.l.c.

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