The Stereochemistry of Organometallic Compounds. Part IX.[1] Sodium Borohydride Reduction of Oxymercury Compounds[2]

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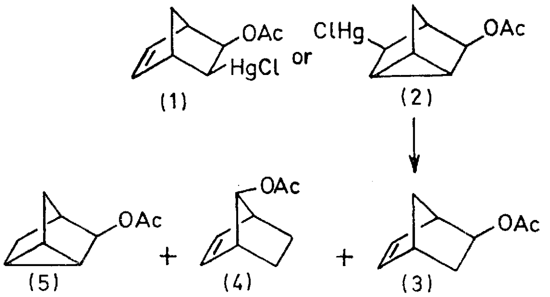
Reduction of either 3-acetoxynorborn-5-en-2-ylmercury(II) chloride (1) or 5-acetoxy-3-nortricyclylmercury(II) chloride (2) with sodium borohydride in tetrahydrofuran gives three acetates: 2-*exo*-acetoxynorborn-5-ene (3), 7-*anti*-acetoxynorborn-2-ene (4), and 3-acetoxynortricyclene (5) in the ratio 8:35:57 (±3). Reduction of (1) with sodium borodeuteride led to stereospecific formation of 5-*exo*-deuterio-substituted (4) but non-stereospecific incorporation of deuterium into the 5-position of compound (5). These results are discussed in terms of the proposed radical mechanism for the reduction of mercurials with borohydride.

Reduction of the acetoxymercurial from 7-propionoxynorbornadiene (9; R = COEt) gives a mixture of the acetoxypropionoxynorbornenes (11 and 12; R = COEt) together with some substituted nortricyclene (13), indicating that a similar rearrangement has occurred.

THE stereochemistry of reduction of 3-acetoxynorborn-5-en-2-ylmercury(II) chloride (1) and 5-acetoxy-3-nortricyclylmercury(II) chloride (2) with sodium borohydride and sodium borodeuteride has been investigated. The mercurials were prepared as described by Pande and Winstein[3] and reduced in aqueous tetrahydrofuran. Three acetates were obtained: 2-*exo*-acetoxynorborn-5-ene (3), 7-*anti*-acetoxynorborn-2-ene (4), and 3-acetoxynortricyclene (5) from reductions with sodium borohydride. The acetates were obtained in high yield and separated by preparative g.l.c. Authentic samples had identical i.r., n.m.r., and mass spectra and g.l.c. retention times. The n.m.r. spectra of (3)[4] and (4),[5] the mass spectra of (3) and (5),[6] and the mass spectrum of (4) as its alcohol[7] were also in agreement with published spectra. Compounds (4) and (5) were hydrolysed to the corresponding alcohols which did not depress the m.p.s of authentic samples. When the reduction procedure of Brown and Geoghegan[8] was used, *i.e.*, without isolation of the intermediate organomercurials, the products were isolated as alcohols in lower yield. Acetylation of a portion of the alcohol mixture followed by g.l.c. analysis showed that the isomer ratio was similar to that before. Reduction of the nortricyclyl mercurial (2) in tetrahydrofuran–deuterium oxide again gave the acetates in similar ratio with no deuterium incorporation, in agreement with the work of Bordwell and Douglass.[9]



(1) (2)

(5) (4) (3)

During the course of this work the results of a similar study of the oxymercuration–reduction of norbornadiene were published.[10] The product ratios were not in agreement with those from our work but reinvestigation of their work by the American authors has now shown that their results are in agreement with ours.[11] Pasto and Gontarz produced strong evidence in favour of a radical mechanism for the reduction of organomercurials by borohydride.[10] Thus our results suggest that the radicals (6), (7), and (8) are in equilibrium. The equilibrium must be fairly rapid as the ratios are insensitive

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[1] Part VIII, W. R. Jackson and T. R. B. Mitchell, *J. Chem. Soc.* (*B*), 1969, 1228.

[2] Most of this work has appeared as a preliminary communication, G. A. Gray and W. R. Jackson, *J. Amer. Chem. Soc.*, 1969, **91**, 6205.

[3] K. Pande and S. Winstein, *Tetrahedron Letters*, 1964, 3393.

[4] J. Paasivirta, *Suomen Kem.*, 1965, **38***B*, 130.

[5] E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, 1964, **86**, 1166.

[6] S. J. Cristol, R. A. Sanchez, and T. C. Morill, *J. Org. Chem.*, 1966, **31**, 2738.

[7] T. Goto, A. Tatematsu, Y. Hata, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron*, 1966, **22**, 2213.

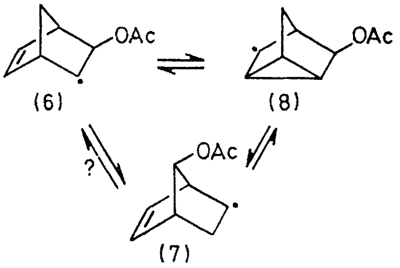
[8] H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, 1967, **89**, 1522.

[9] F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, 1966, **88**, 993.

[10] D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, 1969, **91**, 719.

[11] D. J. Pasto, personal communication.

to reaction conditions and to whether the first formed radical is (6) from (1) or (8) from (2). Equilibrium must therefore be established before the radicals can abstract a hydrogen atom from the borohydride. However, the reaction is not homogeneous and it is thus unwise to speculate on the relative rates of equilibration and hydrogen abstraction. The norbornen-2-yl $\rightleftharpoons$ 3-nortricyclyl radical equilibrium has been studied in homogeneous systems and has been shown to have a rate comparable with that of hydrogen atom extraction from trialkyltin hydrides.[12]



The product ratios are of interest in that they provide another example of the formation of 7-substituted norbornenes from either a 2-substituted norbornenyl radical or a nortricyclyl radical. Although the ready interconversion of radicals of type (6) to type (8) has been demonstrated previously, *e.g.*, where OAc is replaced by SAc,[13] products derived from radicals of type (7) have been observed less frequently. Radical additions to some polychloronorbornadienes have led to 7-substitution but the rearrangement in these cases is encouraged by the formation of an α-chloro-radical, $>\underset{\cdot}{C}-Cl$, in preference to a radical bearing on α-hydrogen atom.[14] Similarly, rearrangements observed in radical additions to hexamethylnorbornadiene involve the formation of a more highly substituted radical.[15] The radical addition of chlorine to benzonorbornadiene also gives some 7-substituted compounds[16] and recently the formation of 7-substituted compounds has been observed in the photochemical addition of cyclohex-2-enone to norbornadiene[17] and in the addition of trimethyltin hydride to norbornadiene.[18]

The stereochemistry of the reaction was investigated by using sodium borodeuteride as a reducing reagent. Reduction of (1) followed by preparative g.l.c. of the product gave small samples of (4) and (5) which were hydrolysed; the n.m.r. spectra (220 MHz) of the corresponding alcohols were recorded. The n.m.r. data are given in the Table.

N.m.r. spectra (220 MHz) of *anti*-7-deuterioxynorbornene in carbon tetrachloride

	2- and 3-H	7-H	1- and 4-H	5- and 6-H (*exo*)	5- and 6-H (*endo*)
τ (non-deuteriated compound)	4·14 (d)	6·58 (s)	7·56br(s)	8·25 (d)	9·05 (d)
		$J_{1,2} = J_{3,4} =$ *ca.* 1 Hz			$J_{exo,endo}$ 1·0 Hz
Integral *	2·00	0·99	1·87	1·96	2·00
τ (deuteriated compound)	4·14 (d)	6·58 (s)	7·56	8·24br(s)	9·05br(d)
Integral •	2·00	0·98	1·85	1·20	1·97

* Average of three determinations, relative to integral for 2- and 3-H which was assumed to be 2·00.

N.m.r. spectra of 3-deuterioxynortricyclene in deuteriobenzene *

	3-H	2-H	4-H	5-H	5-, 6-, and 7-H	1-H
τ (non-deuteriated compound)	6·40 (s)	8·26 (m)	8·36 (s)	8·74 (d)	8·90—8·94 (m)	9·08 (t)
Integral †	1·00	1·02	1·08	1·04	3·95	1·07
τ (deuteriated compound)	6·40 (s)	8·26 (t)	8·36 (s)	8·75br(s)	8·86—8·93 (m)	9·08 (t)
Integral †	1·00	0·95	0·99	0·62	3·34	1·05

* *J* values are not quoted as the spectra appear to be second order. † Average of three determinations, relative to integral for 3-H which was assumed to be 1·00.

Proton assignments for the 7-*anti*-acetate and alcohol have been made previously.[4] The spectrum of the deuteriated product showed that deuterium is almost exclusively incorporated into the 5-*exo*-position. The spectra of the nortricyclanols appeared to be second order at 220 MHz. The proton assignments given are necessarily tentative but additional supporting evidence was obtained from double irradiation experiments for 100 MHz spectra. Irradiation at τ 6·40 (3-H) led to appreciable sharpening of the signals at τ 8·26 and 8·36 (2- and 4-H), and irradiation at τ 9·08 (1-H) led to partial collapse of the multiplet at τ 8·26 (2-H). In the deuteriated sample the intensity of the doublet at τ 8·25 decreased as it collapsed to a broad singlet; the intensity of the low-field end of the multiplet at τ 9·05 also decreased. The ratio of deuterium incorporation was *ca.* 1 : 2 for incorporation at positions corresponding to τ 8·75 and 8·9, respectively. Thus, hydrogen atom abstraction by the radical (8) is non-stereospecific and products with deuterium both *cis* and *trans* to the

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[12] D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1968, **90**, 7047, commenting on the work of C. R. Warner, R. J. Stunk, and H. G. Kuivila, *J. Org. Chem.*, 1966, **31**, 3381.

[13] For leading references see T. V. Van Auken and E. A. Rick, *Tetrahedron Letters*, 1968, 2709; S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, 1968, **90**, 2832.

[14] 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.*, 1498.

[15] E. N. Prilezhaeva, V. A. Asovskaya, G. U. Stepanyanz, D. Mondeshka, and R. J. Shelchtman, *Tetrahedron Letters*, 1969, 4909.

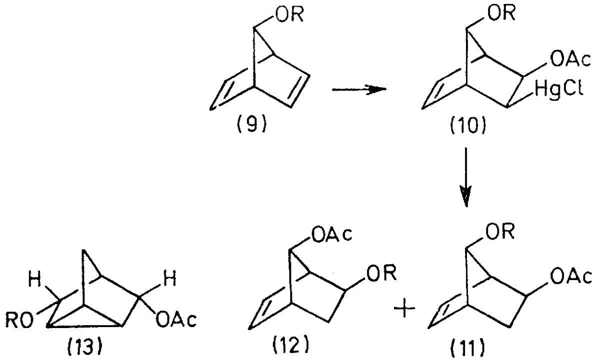
[16] S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, 1967, **32**, 3727.

[17] J. J. McCullough, J. M. Kelly, and P. W. W. Rasmussen, *J. Org. Chem.*, 1969, **34**, 2933.

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

3-acetoxy-group are formed. A similar non-stereospecific chain termination was found by Brace[19] who showed that both *cis*- and *trans*-nortricycyl adducts were formed in the radical addition of iodohexafluoropropane to norbornadiene. In contrast deuterium atom transfer to the 7-acetoxy-radical (7) is highly stereoselective. In the norbornane series, Bordwell and Douglass[9] have reported that reduction of *exo,cis*-3-hydroxynorbornan-2-ylmercury(II) chloride is highly stereoselective, to give the *exo*-2-hydroxy-*exo*-3-deuterio-isomer.

The oxymercuration–sodium borohydride reduction of 7-acetoxynorbornadiene (9; R = Ac) has been reported to give 7-*syn*,2-*exo*-diacetoxynorbornene (11 or 12; R = Ac) and *endo,endo*-3,5-diacetoxynortricyclene (13; R = Ac) in ratio 42 : 58.[20] In this reaction, rearrangements of the type already described, *i.e.* (6) $\rightleftharpoons$ (7) $\rightleftharpoons$ (8) could not be observed as acetoxy-substituted radicals derived from (6) and (7) are enantiomeric and thus gave the same racemic product since the starting material was racemic. The reaction was reinvestigated with sodium borodeuteride as reducing reagent. Two acetates were produced, in similar yield and product ratio to those described by Baird and Buza.[20] The n.m.r. spectrum ($CDCl_3$) of the nortricyclyl diacetate (13; R = Ac) was identical with that described previously[20] except that the integration of the multiplet at τ 8·2—8·8 corresponded to four rather than five protons. There are no stereochemical consequences of deuterium incorporation into the radical precursor of (13) as both C-7 protons are equivalent. The n.m.r. spectrum of deuterio-2,7-diacetoxynorbornene (11 or 12; R = Ac) also resembled the spectrum described previously[20] except that the integration of the large peak τ 8·0—8·2 corresponded to seven rather than eight protons. Spectra in different solvents failed to resolve the signal for the remaining C-3 proton from those of the six acetoxy methyl protons so that a direct assignment of stereochemistry was not possible. Hydrolysis to the corresponding 2,7-diol similarly failed to give unambiguous information, for the 3-*exo*- and 3-*endo*-protons gave an unresolved n.m.r. mu.tiplet at τ 8·30. However, the 2-*endo*-proton in the diacetate gave a doublet at τ 5·3 with some fine structure, with a coupling constant of 8·0 Hz, which is large enough to suggest that *endo*–*endo*-coupling was present and deuterium incorporation had been mainly into the *exo*-position. This assignment must be tentative as differencies between the magnitide of *exo*–*endo* and *endo*–*endo* coupling constants are not always large.[4]



In an attempt to see if rearrangement of the type described was occurring in the 7-substituted norbornadiene system, the acetoxymercuration–sodium borohydride reduction of 7-propionoxynorbornadiene (9; R = COEt)was investigated. An acetoxymercurial (10; R = COEt) was isolated and reduced with sodium borohydride. *cis*-3-Acetoxy-5-propionoxynortricyclene (13; R = COEt) and a norbornene fraction were isolated in ratio 60 : 40, *i.e.*, similar to that in the diacetoxy experiments. The n.m.r. spectrum of the acetoxypropionoxynorbornene fraction showed two acetoxy-resonances at τ 8·26 and 8·30 and pairs of overlapping triplets and quartets at τ 9·1 and 7·9 for the methyl and methylene protons of the propionate group. The spectrum suggests that unrearranged (11; R = COEt) and rearranged (12; R = COEt) have been formed in almost equal amounts. Hydrolysis of the mixture gave pure norbornene-*exo*-2,*anti*-7-diol.

This work thus suggests that sodium borohydride reduction of oxymercurials from both norbornadiene and 7-substituted norbornadienes leads to intermediates which enter equilibria of the type (6) $\rightleftharpoons$ (7) $\rightleftharpoons$ (8) and that hydrogen abstraction by radicals of type (6) and (7) is highly stereoselective in an *exo*-direction whereas a hydrogen abstraction by nortricyclyl radicals (8) is much less stereoselective.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded with a Perkin-Elmer model 137 spectrometer. N.m.r. spectra, except where stated otherwise, were recorded by Mr. R. Spratt and Mr. I. Jack with a Varian HA100 spectrometer for deuteriochloroform solutions with tetramethylsilane as internal standard. Analytical g.l.c. was carried out with a Perkin-Elmer F11 gas chromatograph on a 2-m column of diethyleneglycol succinate (20%) on Chromosorb W. Preparative g.l.c. was carried out with an Aerograph Autoprep A700 with a 20-m column of Apiezon L (30%) on Chromosorb W, 45—60 mesh at 115°. Alumina refers to Peter Spence grade H alumina deactivated by treatment with 5% of aqueous acetic acid (10% by volume).

Materials.—The following materials and reference compounds were prepared by literature methods: *exo*-2-acetoxynorborn-5-ene (3), b.p. 66—70° at 8 mmHg (lit.,[21] 72—74° at 12 mmHg); norborn-5-en-*exo*-2-ol, m.p. 95—99° (lit.,[22] 97·5—99°); 3-acetoxynortricyclene (3-acetoxytricyclo[2,2,1,$0^{2,6}$]heptane) (5), b.p. 72—73° at 8 mmHg, n_D^{25} 1·4686 (lit.,[23] b.p. 83—84° at 13 mmHg), n_D^{25} 1·4681; nortricyclan-3-ol, m.p. 105—109° after sublimation at

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[19] N. O. Brace, *J. Org. Chem.*, 1962, **27**, 3027.

[20] W. C. Baird and M. Buza, *J. Org. Chem.*, 1968, **33**, 4105.

[21] S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Amer. Chem. Soc.*, 1966, **88**, 3087.

[22] J. D. Roberts, E. R. Turnbull, W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, 1950, **72**, 3116.

[23] J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Synth.*, 1965, **45**, 74.

80° and 2 mmHg (lit.,[22] 108—109°); *anti*-7-acetoxynorborn-2-ene (4), b.p. 80° at 15 mmHg, n_D^{25} 1·4670 (lit.,[5] 1·4675); norborn-2-en-*anti*-7-ol, m.p. 116—118° (lit.,[24] 117—118°); 7-acetoxynorbornadiene (9; R = Ac), b.p. 69—74° at 8 mmHg (lit.,[24] 65° at 8 mmHg); 3-acetoxynorborn-5-en-2-ylmercury(II) chloride (1), m.p. 150—152° (decomp.) [(lit.,[3] 152—153° (decomp.)]; 3-acetoxy-5-nortricyclylmercury(II) chloride (2), m.p. 148—149° (lit.,[3] 147—148°).

Sodium Borohydride Reduction of 3-*Acetoxynorborn*-5-*en*-2-*ylmercury*(II) *Chloride* (1).—A suspension of sodium borohydride (1·0 g) in tetrahydrofuran (250 ml) was cautiously added to a stirred suspension of the organomerucy-compound (42 g) in tetrahydrofuran (100 ml) and water (50 ml). The mixture was stirred for a further 30 min and extracted with dichloromethane. The dichloromethane extract was washed with water and dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a colourless liquid (16·0 g). Analytical g.l.c. at 110° showed that three acetates were present: *exo*-2-acetoxynorborn-5-ene (3), *anti*-7-acetoxynorborn-2-ene (4), and 3-acetoxynortricyclene (5), in the ratio 10 : 35 : 57. A mixture of this composition made up from authentic samples gave an identical g.l.c. trace. Preparative gas chromatography at 100° gave pure compounds (4) and (5), identical (i.r., n.m.r., and mass spectra, and g.l.c. retention times) with authentic samples.

Samples of (4) and (5) (500 mg) were hydrolysed with an excess of ethanolic potassium hydroxide solution (4N) for 8 h at room temperature followed by 1 h at reflux. Hydrolysis of (4) gave norborn-2-en-*anti*-7-ol, m.p. 115—117°, mixed m.p. 115—118°. Hydrolysis of (5) gave nortricyclan-3-ol, m.p. and mixed m.p. 105—109° after sublimation at 80° and 2 mmHg.

Two smaller scale reductions of (1) (3·0 g) in tetrahydrofuran (30 ml) with sodium borohydride (0·5 g) in water (5 ml) and tetrahydrofuran (5 ml) gave mixed acetates (1·05 and 1·15 g respectively); g.l.c. analysis showed ratios of (3) : (4) : (5) as 8 : 35 : 57 and 7 : 35 : 58.

Sodium Borodeuteride Reduction of 3-*Acetoxynorborn*-5-*en*-2-*ylmercury*(II) *Chloride*.—A suspension of sodium borodeuteride (1·0 g) in tetrahydrofuran (50 ml) was added cautiously to a stirred suspension of the mercury compound (1) (10 g) in tetrahydrofuran (50 ml) and water (10 ml). The mixture was stirred for a further 30 min and the product (3·7 g, 94%) was isolated as a clear oil in dichloromethane. Preparative g.l.c. at 110° gave samples of (4) and (5) which were shown (n.m.r. spectra) to have incorporated one atom of deuterium per molecule (see Tables in Discussion section).

Sodium Borohydride Reduction of 3-*Acetoxy*-5-*nortricyclylmercury*(II) *Chloride* (2).—Sodium borohydride (1·0 g) in tetrahydrofuran (50 ml) was added cautiously to a stirred suspension of 3-acetoxy-5-nortricyclylmercury(II) chloride (10 g) in tetrahydrofuran (50 ml) and water (10 ml). The mixture was stirred for a further 0·5 h and the product was isolated as a clear oil (4·0 g, 100%) in dichloromethane. Analytical g.l.c. showed the presence of compounds (3), (4), and (5) in the ratio 9 : 35 : 57.

A similar reduction with deuterium oxide (10 ml) in place of water again gave the acetates (3), (4), and (5) in the ratio 9 : 35 : 57; they were separated by preparative g.l.c. In the mass spectra of separate samples of (4) and (5) the intensity of the peak at *m/e* 153 had not increased; their n.m.r. spectra were identical with those of samples obtained from the protium oxide experiment.

Oxymercuration–Demercuration of Norbornadiene.—Norbornadiene (9 g) was treated with mercury(II) acetate (19 g) and then sodium borohydride (75 ml of 3M-solution in aqueous sodium hydroxide) under conditions identical to those described by Brown and Geoghegan.[8] The products were extracted with ether and then hydrolysed with boiling 3N-sodium hydroxide solution (200 ml) for 6 h. The product (3·4 g) was isolated in dichloromethane and the major portion (3·2 g) was chromatographed on silica gel. Elution with light petroleum first gave norborn-2-en-*anti*-7-ol (0·94 g, 8%), m.p. and mixed m.p. 115—118° after sublimation, followed by nortricyclan-3-ol (1·11 g, 9%), m.p. 106—108°, mixed m.p. 105—108° after sublimation. The minor portion of the crude product was acetylated with acetic anhydride–pyridine; g.l.c. analysis of the acetates (0·21 g) showed that (3), (4), and (5) were present in the ratio 5 : 35 : 60.

exo-3,anti-7-*Diacetoxynorborn*-5-*en*-2-*ylmercury*(II) *Chloride* (10; R = Ac).—7-Acetoxynorbornadiene (3·2 g) was added to a suspension of mercury(II) acetate (6·35 g) in acetic acid (14 ml) and the mixture was stirred for 10 min. Sodium chloride was added to the mixture which was then extracted with dichloromethane. The dichloromethane extract was washed with sodium carbonate solution and water and dried ($MgSO_4$), and the solvent was removed to give exo-3,anti-7-*diacetoxynorborn*-5-*en*-2-*ylmercury*(II) *chloride* (8·7 g, 9·4%), m.p. 163—164° (decomp.) (Found: C, 28·8; H, 2·8. $C_{11}H_{12}ClHgO_4$ requires C, 28·4; H, 2·8%); τ 3·74 and 3·90 (q, 5- and 6-H), 4·94 (d, *endo*-2-H), 5·22 (s, 7-H), 6·72 (m, 1-H), 6·86 (m, 4-H), 7·11 [d, *endo*-3-H, $J_{2,3}$(*endo*) 7 Hz], and 7·96 (6H, OAc).

Sodium Borodeuteride Reduction of the Mercurial (10; R = Ac).—The mercurial (7·0 g), suspended in tetrahydrofuran (35 ml) and water (10 ml), was treated with sodium borodeuteride (0·7 g) in tetrahydrofuran (35 ml). The product was isolated in dichloromethane and separated into a pentane-soluble and a pentane-insoluble product. Recrystallisation of the former from pentane gave *exo*-2,*anti*-7-diacetoxynorborn-5-ene (11 or 12; R = Ac) (0·8 g) which was chromatographed on a silica gel column in ether–light petroleum (1 : 4) to give a pure sample (0·6 g), m.p. 32—35° (lit.,[20] 30—35°); τ (C_6D_6) 4·36 (m, 5- and 6-H), 5·33 (dd, 2-H), 5·50 (d, 7-H), 6·87 (m, 1-H), 7·5 (m, 4-H), and 8·2—8·4 (7H, m, 3-H and OAc). The pentane-insoluble product was recrystallised from cyclohexane to give *endo*,*endo*-2,5-diacetoxynortricyclene (13; R = Ac) (0·1 g), m.p. 106—108° (lit.,[20] 106—108°); τ (C_6D_6) 5·2 (s, 3- and 5-H), 7·68 (s, 4-H), 8·20 (s, OAc), 8·60 (d, 2- and 6-H, $J_{1,2} = J_{2,6} =$ 6·5 Hz), 8·97 (s, 5-H), and 9·14 (t, 1-H). G.l.c. analysis of a sample of the crude product showed that the diacetoxynorbornenes and -nortricyclenes were present in the ratio 44 : 56.

Hydrolysis of 3-*Deuterio*-exo-2,anti-7-*diacetoxynorborn*-5-*ene*.—The deuteriated acetate (0·6 g) was set aside overnight with 10% ethanolic potassium hydroxide solution (15 ml). The product was isolated in ethyl acetate and sublimed at 110° and 0·6 mmHg, to give *deuterionorborn*-5-*ene*-exo-2,anti-7-*diol* (0·13 g), m.p. (sealed capillary) 117—120° (Found: C, 66·5; H + D, 8·7. $C_7H_9O_2D$ requires C, 66·1; H + D, 8·7%); * τ [$(CD_3)_2CO$] 3·94 (octet, 5-H), 4·14 (octet, 6-H), 6·16—6·22 (m, 7-H and *endo*-2-H), 7·44 (m, 1- and 4-H), and 8·30 (q, 3-H).

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* Reproducible analyses could not be obtained for this compound.

[24] P. R. Story, *J. Org. Chem.*, 1961, **26**, 287.

A sample of this diol which did not contain deuterium was obtained by reduction of the mercurial (10; R = Ac) by sodium borohydride followed by hydrolysis of the *exo*-2,*anti*-7-diacetoxynorborn-5-ene. Sublimation of the crude product at 110° and 0·6 mmHg gave the diol, m.p. 115—119° (sealed capillary). The n.m.r. spectrum $[(CD_3)_2CO]$ was identical to the foregoing spectrum except that the absorption at τ 8·3 was a multiplet (2H).

exo-3-*Acetoxy*-anti-7-*propionoxynorborn*-5-*en*-2-*ylmercury*-(II) *Chloride* (10; R = COEt).—7-Propionoxynorbornadiene (9; R = COEt) (4·2 g) was added to a stirred suspension of mercury(II) acetate (7·5 g) in acetic acid (16 ml) and the mixture was stirred for a further 10 min. The mercurial was precipitated by the addition of salt and recrystallised from chloroform–light petroleum to give exo-3-*acetoxy*-anti-7-*propionoxynorborn*-5-*en*-2-*ylmercury*(II) *chloride* (9·5 g, 67%), m.p. 126—128° (Found: C, 31·4; H, 3·5. $C_{12}H_{15}ClHgO_4$ requires C, 31·4; H, 3·3%).

Sodium Borohydride Reduction of the Mercurial (10; R = COEt).—Sodium borohydride (0·7 g) in tetrahydrofuran (40 ml) was added to a stirred suspension of the mercurial (7·0 g) in a mixture of tetrahydrofuran (40 ml) and water (6 ml). The mixture was stirred for a further 0·5 h and the product was isolated in dichloromethane. The mixture was chromatographed on silica gel. Elution with ether–pentane (1 : 9) gave a clear oil (0·9 g, 26%) which was shown to be a 50 : 50 mixture of *anti*-7-acetoxy-*exo*-2-propionoxynorborn-5-ene (12; R = COEt) and *exo*-2-acetoxy-*anti*-7-propionoxynorborn-5-ene (11; R = COEt) (*Found*: C, 64·4; H, 7·3. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·2%); τ (C_6D_6) 8·26 and 8·30 (s of almost equal intensity, Ac), 9·1 (overlapping triplets, EtCO), and 7·9 (overlapping quartets, EtCO) together with the usual norbornene multiplet absorptions at τ 4·4 (5- and 6-H), 5·30 (2-H), 5·45 (7-H), 6·81 (1-H), 7·50 (4-H), and 8·26 (3-H), partially obscured by Ac absorption. Further elution with the same solvent system gave cis-endo, endo-3-*acetoxy*-5-*propionoxynortricyclene* (13; R = COEt) (1·25 g, 36%) as white needles, m.p. 67—68°, unchanged after crystallisation from ether (Found: C, 64·7; H, 7·5%); τ (C_6D_6) 8·24 (s, Ac), 7·88 (q, EtCO), 9·0 (t, EtCO), 5·28 (s, 3- and 5-H), 7·70 (s, 4-H), 8·63br (d, 2- and 6-H, $J_{1,2}$ 6·5 Hz), *ca.* 9·0 (m, 7-H, partially obscured by Ac absorption), and 9·20 (t, 1-H).

Hydrolysis of the Acetoxypropionoxynorbornene Mixture (11 and 12; R = COEt).—The ester mixture (0·47 g) was set aside overnight with 10% methanolic potassium hydroxide solution (7 ml). The volume of the solution was reduced to 2 ml under reduced pressure and a saturated solution of sodium chloride was added. The mixture was extracted with dichloromethane (5 × 20 ml), and the extract was washed once with saturated brine, dried $(MgSO_4)$, and evaporated to give a yellow semi-solid (225 mg). G.l.c. of this product at 185° on a Versamid 900 column showed a single peak coincident with that of an authentic sample of norborn-5-ene-*exo*,*anti*-2,7-diol. The crude product was sublimed at 100° and 2 mmHg to give a pure sample of the diol, m.p. 115—117°, mixed m.p. 116—119° with an authentic sample prepared by hydrolysis of the diacetate.

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