Dehydrobromination of 3-Bromotricyclo[5.3.1.0^{3,8}]undecane (3-Bromo-4-homoisotwistane) and Some Addition Reactions of Tricyclo[5.3.1.0^{3,8}]-undec-2-ene. Stereochemistry of the Formation and Reaction of an Anti-Bredt Compound probed by Deuterium Substitution

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3-Bromotricyclo[5.3.1.0^{3,8}]undecane (2) is easily dehydrobrominated with sodium amide in refluxing toluene to give tricyclo[5.3.1.0^{3,8}]undec-2-ene (3), an anti-Bredt compound, in 52% yield. The olefin (3) obtained from the 2-*exo*-deuterio-derivative of the bromo-compound (2) was almost free from deuterium, indicating a predominant *exo,syn*-mechanism for dehydrobromination. Both acid-catalysed addition of water and oxymercuration of (3) proceeded highly regioselectively with exclusive formation of the 3-alcohol (4), whereas hydroboration of (3) proceeded with less regioselectivity. Use of deuteriated reagents for hydration and oxymercuration–demercuration of (3) and subsequent conversion of the product alcohol (4) into the olefin (3) *via* the bromide (2) revealed that water underwent addition with an almost pure *exo,syn*-mechanism, whereas mercury(II) acetate reacted with a mixed *syn*- and *anti*-mechanism. The predominant factor in determining the stereochemistry (complete *exo,syn*) of the acid-catalysed hydration of (3) is suggested to be electronic in nature, consisting of an uneven distribution of π-electrons between the *exo*- and *endo*-sides of the olefin (3).

SINCE Wiseman's experiment on the debromination of 1,2-*exo*-dibromobicyclo[3.3.1]nonane to bicyclo[3.3.1]-non-1-ene,[1] an *exo,syn*-elimination mechanism seems to have been considered self-evident for the formation of anti-Bredt compounds from a variety of bridgehead derivatives of bicyclic compounds comprising small- to medium-sized rings.[2] This is in fact highly probable, in view of the apparent impossibility of these compounds assuming *anti*-elimination transition states, because of the rigidity of the molecular framework.

The first positive evidence for *syn*-elimination came out recently in the work of Khim and White,[3] in which only the *cis*-isomer of an *N*-sulphoxyimino-oxazoline-fused bicyclo[3.3.1]nonane gave the corresponding anti-Bredt compound. We present here further experimental evidence for the *syn*-elimination mechanism, as demonstrated in the dehydrobromination of 3-bromotricyclo-[5.3.1.0^{3,8}]undecane (3-bromo-4-homoisotwistane) (2)[4] to the 2-ene (3).[5] This reaction is considered particularly suitable as a probe to clarify the elimination mechanism, because the dehydrobromination is highly regiospecific, giving neither the 3(4)-ene nor the 3(8)-ene as by-products, and because the 2-*exo*-hydrogen atom, which is to be eliminated if the *syn*-mechanism is operating, is rigidly held *cis* to the leaving 3-bromine atom.

We hoped to distinguish between *syn*- and *anti*-eliminations in this dehydrobromination by conducting the reaction with a 3-bromide (2) in which one of the 2-hydrogen atoms had been replaced by deuterium. A sample of epimerically pure 3-bromo-2-*exo*-deuterio-derivative, [2-*exo*-^{2}H]-(2) (isotopic purity 89%), was synthesized[6] by hydroboration of the 2-ene (3) with sodium borodeuteride followed by reaction with thionyl bromide (see Scheme).

Hydroboration of the olefin (3) has been found[5] to proceed with low regioselectivity to give 23% 3-ol (4) and 77% 2-*exo*-ol (5). The stereospecificity of the reaction, however, was quite high, no 2-*endo*-ol being obtained. The absence of the 2-*endo*-ol was demonstrated by comparison of the product alcohols with an authentic specimen of the 2-*endo*-ol, prepared from the 2-*exo*-ol (5) through Jones oxidation followed by reduction with lithium aluminium hydride. Deuterioboration of the olefin (3) afforded only slightly different proportions of the two isomeric alcohols: 26% 2-*exo*-deuterio-3-ol and 74% 3-deuterio-2-*exo*-ol. The *exo*-configuration of the 2-deuterium atom in the alcohol [2-*exo*-^{2}H]-(4) was assumed in the light of the above-mentioned exclusive *exo,syn*-attack of diborane on the olefin (3). The configuration was expected to be retained during the reaction with thionyl bromide, in which substitution occurred on the carbon atom β to the deuterium. This inference is supported indirectly by the fact that the deuterium content (89%) remained unchanged throughout the conversion from the alcohol [2-*exo*-^{2}H]-(4) into the bromide [2-*exo*-^{2}H]-(2) and then into the hydrocarbon [2-*exo*-^{2}H]-(1). This last reaction was achieved with lithium metal in t-butyl alcohol.[4] The fact that the content of deuterium in the hydrocarbon [2-*exo*-^{2}H]-(1) was the same as in the original alcohol [2-*exo*-^{2}H]-(4) indicates that the content of isotope in the bromide [2-*exo*-^{2}H]-(2) is also the same.†

The 2-*exo*-deuterio-bromide [2-*exo*-^{2}H]-(2) prepared in this way was dehydrobrominated by treatment with sodium amide in refluxing toluene for 2 h. The resulting 2-ene was examined by g.l.c.–mass spectrometry, and found to contain only 0.3% of the 2-deuterio-olefin [2-^{2}H]-(3) after correction for natural abundance carbon

† Direct measurement of the deuterium content of the bromide [2-*exo*-^{2}H]-(2) by mass spectrometry was rendered inaccurate because of the low intensities of the parent peaks, arising from easy ionization as well as from the isotopic heterogeneity of the bromine.

[1] J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, 1970, **92**, 956.

[2] (*a*) G. L. Buchanan, *Chem. Soc. Rev.*, 1973, **3**, 41; (*b*) G. Köbrich, *Angew. Chem. Internat. Edn.*, 1973, **12**, 464.

[3] M. Khim and J. D. White, *J. Amer. Chem. Soc.*, 1975, **97**, 451.

[4] N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, K. Aigami, and E. Ōsawa, *J.C.S. Chem. Comm.*, 1975, 371.

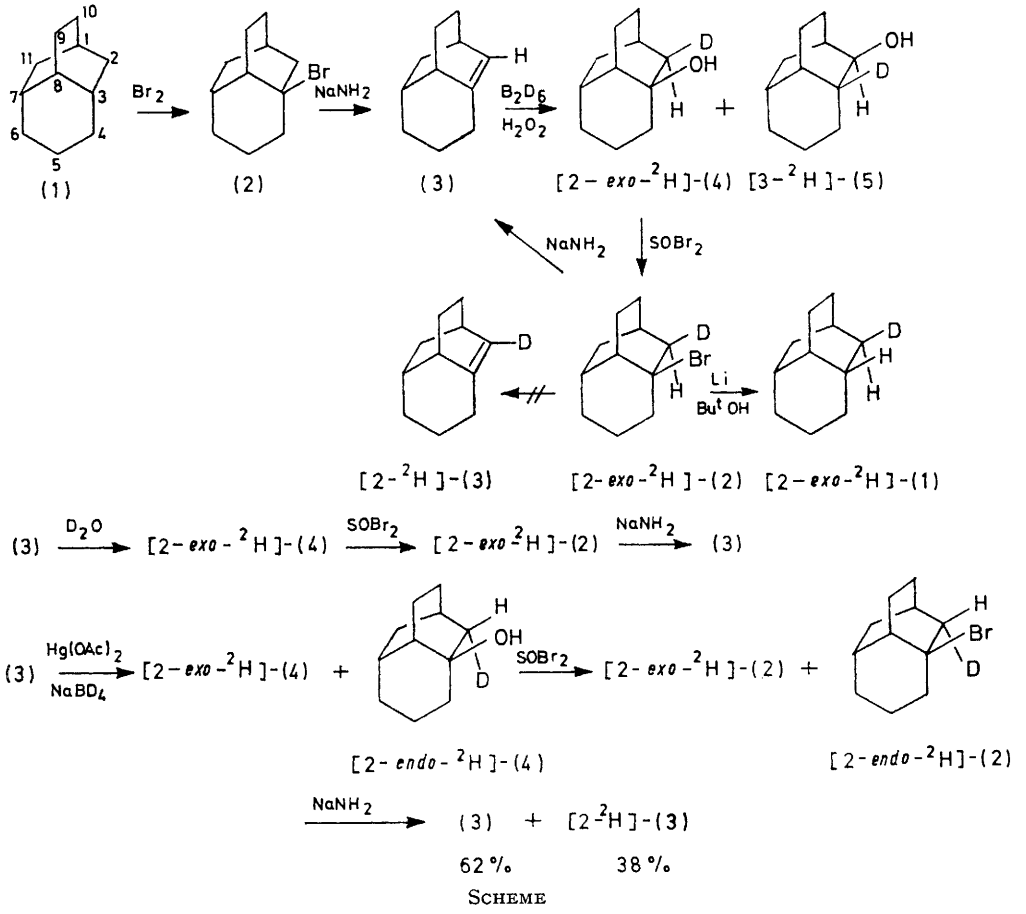
[5] N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, and K. Aigami, *J.C.S. Chem. Comm.*, 1975, 372.

[6] Y. Fujikura, Y. Inamoto, N. Takaishi, H. Ikeda, and K. Aigami, *Chem. Letters*, 1975, 1203.

and hydrogen isotopes and mass spectrometric recombination effect.

The content of [2-^{2}H]-(3) in the product olefin is related directly to the rate ratio for the *syn*- and *anti*-elimination reactions, since the possibility of the secondary conversion of [2-^{2}H]-(3) into (3) was excluded on the basis of no loss in deuterium from a mixture of (3) and [2-^{2}H]-(3) (obtained in the oxymercuration described below) on prolonged heating with sodium amide. The figure of 0.3% [2-^{2}H]-(3) corresponds to a rate of *syn*-elimination about 300 times larger than that of *anti*-elimination. This rate ratio would be larger for the non-deuteriated bromide (2), in view of the nature of primary and secondary deuterium isotope effects.

Only a few addition reactions of anti-Bredt compounds seem to have been studied so far.[1,5,7] Addition of bromine to bicyclo[3.3.1]non-1-ene showed complete *exo,syn*-stereochemistry,[1] whereas hydroboration of the same olefin gave a small amount of 2-*endo*-hydroxy-product.[7] This difference, coupled with the exclusive *exo*-hydroboration of (3) described above, encouraged us to examine other addition reactions of the olefin (3). Acid-catalysed hydration and oxymercuration were attempted, since the former was found,[5] and the latter was expected,[8-10] to give with high regioselectivity the 3-ol (4), which could be transformed back into the original olefin (3) *via* the bromide (2). Use of deuterium oxide and sodium borodeuteride for hydration and demercuration, respectively, would result in incorporation of deuterium into the alcohol (4) in the configuration corresponding to the mechanism (*syn* or *anti* from the *exo*- or the *endo*-side) of the addition reaction. As demonstrated above, these configurations of the deuterium atom in the product alcohol (4) are retained on treatment with thionyl bromide, and only a deuterium atom at the 2-*exo*-position is eliminated on subsequent dehydrobromination. Therefore, the extent of retention of deuterium in the final olefin (3) should be a direct measure of the extent of *syn*- or *anti*-mechanism in these addition reactions.



SCHEME

Treatment of the olefin (3) with deuterium oxide con-

[7] J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, 1970, **92**, 948.

[8] T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, 1963, **85**, 2746; T. G. Traylor, *ibid.*, 1964, **86**, 244; *Accounts Chem. Res.*, 1969, **2**, 152.

[9] H. C. Brown and W. J. Hammar, *J. Amer. Chem. Soc.*, 1967, **89**, 1524; H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, 1967, **89**, 1525; H. C. Brown and J. H. Kawakami, *ibid.*, 1970, **92**, 201; H. C. Brown and K.-T. Liu, *ibid.*, 1971, **93**, 7335; H. C. Brown, J. H. Kawakami, and K.-T. Liu, *ibid.*, 1973, **95**, 2209; H. C. Brown, P. J. Geoghegen, jun., G. J. Lynch, and J. T. Kurek, *J. Org. Chem.*, 1972, **37**, 1941.

[10] N. Takaishi, Y. Fujikura, and Y. Inamoto, *J. Org. Chem.*, 1975, **40**, 3767.

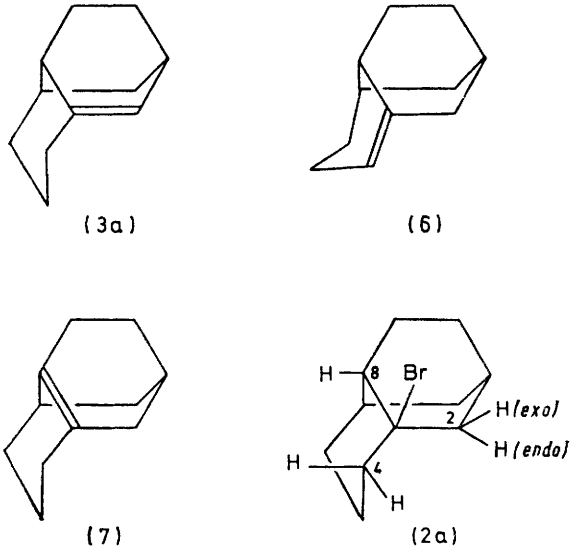
taining a small amount of deuteriosulphuric acid yielded exclusively the 2-deuterio-3-ol [2-^{2}H]-(4) (isotopic purity 86%). The final bridgehead olefin obtained from this contained only 0.6% [2-^{2}H]-(3), corresponding to almost complete *exo,syn*-addition of deuterium oxide to the olefin (3).

Oxymercuration of the olefin (3) with mercury(II) acetate in aqueous tetrahydrofuran at room temperature was complete in a few minutes. Demercuration with sodium borodeuteride gave the 2-deuterio-3-ol [2-^{2}H]-(4) in 86% yield, in which no 2-hydroxy-isomer was detected by g.l.c.–mass spectrometry. Thus the oxymercuration also proceeds quite regiospecifically. Dehydrobromination of the bromide [2-^{2}H]-(2) from this sample of [2-^{2}H]-(4) led to a mixture of 38% deuterio-olefin [2-^{2}H]-(3) and 62% non-deuteriated analogue (3). This indicates that, in contrast to hydration, oxymercuration proceeds with mixed *syn*- and *anti*- (57 and 43%, respectively) additions of Hg^{2+} and nucleophile. No 3-acetate was detected in the oxymercuration–demercuration product, although acetates have been reported to be invariably associated with the *syn*-mechanism.[8]

DISCUSSION

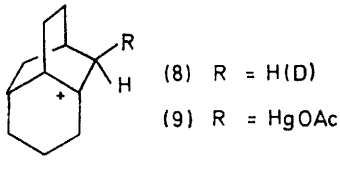
The regiospecificity and the *syn*-elimination mechanism in dehydrobromination of the bromide (2) are in good agreement with the thermodynamic [11a] and the kinetic [11b] expression of Wiseman's selectivity rule for the formation of anti-Bredt compounds. Dreiding models indicate that the 2-ene (3) [see (3a)] would be the most stable of the three possible bridgehead 3-olefins [(3), (6), and (7)]. Selective elimination of H-2-*exo* can be visualized with reference to structure (2a): only this hydrogen atom is *cis*, and the others (H-2-*endo*, H-4, and H-8) are at a dihedral angle of 120° or *gauche* to the leaving bromine atom. Thus the rigidly held, eclipsed conformation for C-2 and C-3 offers an ideal arrangement of the 3-bromine and the 2-*exo*-hydrogen atom for a *syn*-elimination transition state.

Extremely high regio- and stereo-selectivity in acid-catalysed hydration of the olefin (3) is considered to be characteristic of the structure and reactivity of anti-Bredt compounds. This feature could arise from an uneven π-electron distribution caused by the pyramidal electronic structure of the bridgehead olefinic carbon atom. The occurrence of pyramidal hybridization of an olefinic carbon atom has been established in certain strained cyclic olefins.[12] Deviation from a planar electronic configuration is a compromise result of the changes in hybridization, orbital overlap, and torsional energies in order to minimize the total molecular energy.[2a,12] The same situation should hold with anti-Bredt compounds, in which a large increase in torsional energy is expected if their bridged molecular frameworks are distorted so as to maintain the planar configuration of the bridgehead olefinic carbon atoms. A pyramidal bridgehead olefinic carbon atom is necessarily associated with an uneven



π-electron distribution with respect to the *exo*- and *endo*-sides of the molecule, with a greater electron density on the *exo*-side.

We regard, in agreement with Fukui,[13] electronic rather than steric factors as more important in determining the stereoselectivity in the hydration of the olefin (3). The regiochemistry of hydration of (3) * and the great stability of the 3-cation (8) [4] strongly suggest that acid-catalysed hydration of (3) is a unimolecular process involving slow protonation to form the unstable intermediate (8). Both *exo*- and *endo*-attack of a proton at



C-2, corresponding to *syn*- and *anti*-hydration, respectively, give the same intermediate (8). Steric hindrance to the approach of the proton would be the same and small on either side of (3). The electronic effect, therefore, should be the predominant factor in determining the activation energy, and it must be smaller for proton attack on the more electron-rich, *exo*-side.

The intermediate for the oxymercuration of the olefin (3) is probably an open cation with a σ-bonded mercury atom such as (9), rather than a mercury-bridged (ethylenemercurio-) type, as established for strained cyclic olefins.[8,9] The open cation (9) seems rational because of

* The same orientation of the reagent was found in our recent study on the addition of keten to the olefin (3), giving tetracyclo[7.3.1.0^{2,5}.0^{5,10}]tridecan-3-one as the only product.[14]

[11] (*a*) J. R. Wiseman, *J. Amer. Chem. Soc.*, 1967, **89**, 5966; (*b*) J. R. Wiseman, H.-F. Chan, and C. J. Ahola, *ibid.*, 1969, **91**, 2812.

[12] N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, 1972, **94**, 5734.

[13] K. Fukui and H. Fujimoto, *Tetrahedron Letters*, 1965, 4303; 1966, 5551.

[14] N. Takaishi, Y. Fujikura, Y. Inamoto, and H. Ikeda, *Chem. Letters*, 1975, 957.

the tendency towards charge localization at C-3, as indicated by the stability of the cation (8). This is also supported by the absence of acetate [8] in the present oxymercuration–demercuration product. In addition, an *endo*-mercury-bridged ion cannot be the intermediate precursor of the 2-*endo*-deuterio-product [2-*endo*-^{2}H]-(4), because the *endo*-bridged ion must be too strained to have a finite existence.

In the light of this postulation of the open cation (9) (and its *endo*-mercurio-epimer), the ratio of *exo*-, [2-*exo*-^{2}H]-(4), to *endo*-product, [2-*endo*-^{2}H]-(4), should represent that of *exo*- to *endo*-attack of Hg^{2+} on C-2 atom of the olefin (3). Apparently this result cannot be interpreted in terms of uneven distribution of electrons in (3), which predicts predominant *exo*-attack. Steric retardation for the *exo*-approach of Hg^{2+} is the remaining possibility. It might be thought that steric hindrance is not an adequate explanation of decreased *exo*-addition, since bi- and poly-cyclic olefins are generally more congested on the *endo*-side.* However, this may not necessarily be the case for (3), if we take into account the fact that the molecule (3) is probably appreciably distorted from the planar-symmetric tricycloundecane framework. It is quite possible that steric hindrance close to C-2 in the olefin (3) is larger on the *exo*- than on the *endo*-side.

EXPERIMENTAL

Instruments for i.r., ^{1}H n.m.r., and mass spectra, conventional and preparative g.l.c., and Golay g.l.c.–mass spectrometry were as used previously.[15]

Sodium borodeuteride (above 98% purity), deuterium oxide (99.9%), and 98% [$^2H_2$]sulphuric acid (above 99%) were commercial (Merck). Tricyclo[5.3.1.0^{3,8}]undecane (1),[16] its 3-bromo-derivative (2),[17] and the 2-ene (3) [17] were prepared as described previously.

Deuterioboration of Tricyclo[5.3.1.0^{3,8}]*undec-2-ene* (3).—A mixture of the 2-ene (3) (6.23 g, 4.21 mmol), sodium borodeuteride (0.55 g, 13.0 mmol), and sodium-dried tetrahydrofuran (20 ml) was treated with boron trifluoride–ether complex (2.1 ml, 16.8 mmol) in tetrahydrofuran (20 ml), and then with 3N-sodium hydroxide (8 ml) and 35% hydrogen peroxide (7.2 ml) (procedure as in ref. 17). The product (94% yield) comprised 26% 2-*exo*-deuterio-3-ol [2-*exo*-^{2}H]-(4) and 74% 3-deuterio-2-*exo*-ol [3-^{2}H]-(5). The less abundant component was separated by preparative g.l.c. to give a pure sample, $\nu_{max.}$ 2 170 and 2 180 cm^{-1} (C–D), *m/e* 167 (100%, M^+), 149 (42), 110 (31), 97 (79), 96 (94), 95 (45), 84 (42), 79 (40), 67 (30), and 41 (47).

The deuterium content of the [2-*exo*-^{2}H]-(4) thus obtained was calculated to be 89% from the formula $1 - a/[(b - fa) + a]$, where a (intensity of the peak for *m/e* 166) = 41 and b (that for *m/e* 167) = 331. The factor f is the ratio of intensities of the $M + 1$ peak and the molecular ion (M) peak for the protium compound.[18] This is introduced to correct for the effect of natural abundance hydrogen and carbon isotopes; the value of f for the alcohol (4) ($C_{11}H_{18}O$) is 0.1221.[18]

The more abundant component, [3-^{2}H]-(5), of the deuterioboration product mixture, similarly purified, showed $\nu_{max.}$ 2 140 and 2 160 cm^{-1}, *m/e* 167 (40%, M^+), 149 (100), 136 (87), 92 (65), 91 (36), 81 (35), 80 (36), 79 (42), 67 (41), and 41 (47).

3-*Bromo*-2-exo-*deuteriotricyclo*[5.3.1.0^{3,8}]*undecane*, [2-exo-^{2}H]-(2).—A mixture of the 2-*exo*-deuterio-3-ol [2-*exo*-^{2}H]-(4) (2.23 g, 13.0 mmol) obtained above, freshly distilled thionyl bromide (3 ml), and dry benzene (7 ml) was refluxed for 2 h. Most of the solvent and the excess of thionyl bromide were evaporated off under diminished pressure, and the residue was diluted with carbon tetrachloride (5 ml). The solution was washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. The residue was purified by preparative g.l.c. to give a pure sample [2-*exo*-^{2}H]-(2), $\nu_{max.}$ 2 160 cm^{-1}, *m/e* 150 (100), 149 (72), 120 (67), 119 (49), 92 (58), 91 (49), 80 (49), 79 (56), 67 (42), and 39 (33).

Reduction of the 3-*Bromo*-2-exo-*deuterio-derivative* [2-*exo*-^{2}H]-(2).—The crude 3-bromide (1.50 g, 6.5 mmol) obtained above was dissolved in tetrahydrofuran (10 ml) and t-butyl alcohol (10 ml), and lithium metal (0.6 g, 87 mmol) was added in small portions at ambient temperature. More t-butyl alcohol (3 ml) was added, and the mixture was refluxed for 3 h. Methanol (3 ml) and water (20 ml) were then added, and the mixture was extracted with n-pentane (5 × 10 ml). The extract was washed with water, dried ($MgSO_4$), and concentrated. The residue was purified by sublimation *in vacuo* to give the hydrocarbon [2-exo-^{2}H]-(1),[16] m.p. 62—63°, $\nu_{max.}$ 2 150 cm^{-1}, *m/e* 151 (100, M^+), 123 (30), 122 (41), 108 (24), 94 (28), 81 (40), 80 (42), 79 (30), 67 (36), and 41 (22), isotopic purity 89% (calculated as above with $a = 61$, $b = 529$, and $f = 0.1218$).[18]

Dehydrobromination of the 3-*Bromo*-2-exo-*deuterio-derivative* [2-*exo*-^{2}H]-(2).—The 3-bromide (1.50 g, 6.5 mmol) was treated with sodium amide (0.5 g, 12.8 mmol) in refluxing toluene (10 m) for 2 h.[17] Filtration and evaporation gave the crude 2-ene (3) (0.4 g, 41%). A purified sample (g.l.c.) showed a mass spectrum almost identical with that of the non-deuteriated compound: [17] *m/e* 148 (43%, M^+), 94 (100), 92 (18), 91 (42), 79 (63), 77 (20), 41 (21), 39 (21), 28 (15), and 18 (18), and no C–D stretching i.r. absorption was observed.

The proportion of 2-deuterio-olefin [2-^{2}H]-(3) was calculated to be 0.3% (as above, with $a = 125$, $b = 19$, and $f = 0.149$). Since this value is of the same order of magnitude as that of the experimental error in the measurement of intensity (0.5%), practically no 2-*exo*-deuterium is retained in the dehydrobromination reaction. The value for f of 0.149, rather than 0.1214 (the calculated value for $C_{11}H_{16}$ [18]), is that found experimentally for the non-deuteriated olefin (3). The deviation from the calculated value may be attributed to recombination of the olefin (3) with a proton to give a stable 3-cation, which has the same *m/e* value (149) as the $M + 1$ peak of (3).

Addition of Deuterium Oxide to Tricyclo[5.3.1.0^{3,8}]*undec-2-ene* (3) *in the Presence of Deuteriosulphuric Acid.*—A mixture of the 2-ene (3) (3.13 g, 21.1 mmol), deuterium oxide (10 g), dry acetone (15 ml), and the deuteriosulphuric acid (0.01 g) was stirred at ambient temperature for 2 h, diluted with

* *Cf.* ref. 9 and references cited in refs. 5 and 10.

[15] N. Takaishi, Y. Inamoto, and K. Aigami, *J.C.S. Perkin I*, 1975, 789.

[16] N. Takaishi, Y. Inamoto, K. Aigami, K. Tsuchihashi, and H. Ikeda, *Synth. Comm.*, 1974, **4**, 225; N. Takaishi, Y. Inamoto, and K. Aigami, *J. Org. Chem.*, 1975, **40**, 276.

[17] K. Aigami, Y. Inamoto, N. Takaishi, Y. Fujikura, A. Takatsuki, and G. Tamura, *J. Medicin. Chem.*, 1976, **19**, 563.

[18] R. M. Silverstein and G. C. Bassler, ' Spectroscopic Identification of Organic Compounds,' Wiley, New York, 1963, p. 28.

water (50 ml), and extracted with n-hexane (5 × 10 ml). The combined extracts were washed with water and dried (Na_2SO_4). Evaporation gave crude 2-*exo*-deuterio-3-ol [2-*exo*-^{2}H]-(4) (2.94 g, 83%). Preparative g.l.c. gave a sample, $\nu_{max.}$ 2 170 and 2 180 cm^{-1}, *m/e* 167 (72%, M^+), 149 (20), 110 (27), 97 (65), 96 (76), 95 (35), 84 (37), 79 (33), 67 (26), 41 (37), and 18 (100), isotopic purity 86% (as above with $a = 14$, $b = 91$, and $f = 0.1221$ [18]).

The crude product was treated with thionyl bromide; preparative g.l.c. gave the deuterio-bromide [2-*exo*-^{2}H]-(2), $\nu_{max.}$ 2 160 cm^{-1}, *m/e* 150 (100), 149 (20), 94 (23), 91 (20), 81 (21), 80 (18), 79 (31), 68 (21), 67 (40), and 41 (18). Dehydrobromination of this sample gave the olefin (3) containing 0.6% of deuterio-compound [2-^{2}H]-(3) (calculated with $a = 442$, $b = 69$, and $f = 0.149$). The absence of deuterium was also indicated by its i.r. spectrum.

Oxymercuration–Demercuration (by Sodium Borodeuteride) of the Olefin (3).—The 2-ene (3) (3.0 g, 20 mmol) was added to a suspension of mercury(II) acetate (6.38 g, 20 mmol) in tetrahydrofuran (15 ml) and water (20 ml), and the mixture was stirred at ambient temperature. The yellow colour faded in 4 min and 3N-sodium hydroxide (20 ml) was added, followed by sodium borodeuteride (0.42 g, 10 mmol) in 3N-sodium hydroxide (20 ml). After being saturated with sodium chloride, the mixture was extracted with ether (5 × 20 ml). The combined extracts were washed with water and dried (Na_2SO_4). Evaporation left the crude 2-deuterio-3-ol [2-^{2}H]-(4) (2.86 g, 86%), which showed only one peak on g.l.c.–mass spectrometry. Slow sublimation under diminished pressure gave a pure sample,[17] m.p. 104—104.5°, $\nu_{max.}$ 2 160 cm^{-1}, *m/e* 167 (100), 110 (36), 97 (77), 96 (44), 95 (48), 84 (42), 79 (32), 67 (28), 41 (43), and 18 (43), isotopic purity 89% (as above, with $a = 17$, $b = 143$, and $f = 0.1221$[18]). Treatment with thionyl bromide yielded [2-^{2}H]-(2), $\nu_{max.}$ 2 160 cm^{-1}, *m/e* 150 (100), 149 (47), 120 (19), 93 (14), 92 (19), 91 (18), 81 (17), 80 (15), 79 (26), and 67 (21), which was dehydrobrominated to the olefin (3), $\nu_{max.}$ 3 020 (:CH) and 2 240 cm^{-1} (:CD), *m/e* 149 (34), 148 (46), 95 (54), 94 (100), 93 (27), 92 (44), 91 (47), 80 (41), 79 (62), and 77 (33). The i.r. spectrum clearly indicated the presence of an olefinic deuterium atom, and the mass spectrum was different from that of pure (3). The content of deuterio-olefin [2-^{2}H]-(3) was calculated as above ($a = 216$, $b = 162$, and $f = 0.149$) to be 38%. Since the isotopic purity of the 2-deuterio-3-ol [2-^{2}H]-(4) was 89%, the presence of 38% of [2-^{2}H]-(3) in this sample corresponds to 43% *anti*- and 57% *syn*-addition in the oxymercuration.

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