Reactions over Metal Catalysts. Part I. The Stereochemistry of Hydrogenolysis of 3-Acetoxynortricyclene [1]

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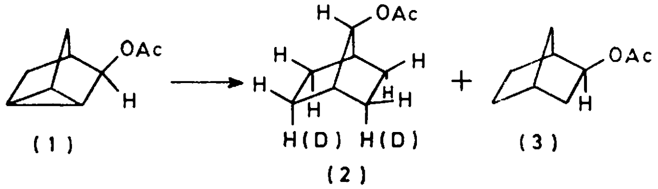
Hydrogenolysis of 3-acetoxynortricyclene gives a mixture of acetoxynorbornanes in which 7-acetoxynorbornane predominates. When deuterium is used in the reaction, the n.m.r. spectra of this product shows a stereospecific deuterium incorporation into 2,6-*endo*-positions. The reactions of acetoxyquadricyclene and 7-acetoxynorbornadiene with deuterium are also discussed.

THE stereochemistry of hydrogenolysis of cyclopropane rings has been the subject of much recent interest.[2-4] In the first unambiguous study of stereochemistry, Majerski and Schleyer [3] showed that hydrogenolysis of tricyclo[4.4.1]undecane gave an almost equal mixture of *cis*- and *trans*-1-methyltricyclo[4.4.0]decanes in a very non-stereoselective fashion. In contrast, Indian workers [4] have produced an example of cyclopropane ring hydrogenolysis in the gibbane series which is stereospecifically *trans*. Kieboom and his co-workers [2] have pointed out that both of these results together with those reported by us,[1] could be explained in terms of a stereospecific *suprafacial* addition of hydrogen. They in turn looked at the hydrogenolysis of *trans*-1,2-dimethyl-1,2-diphenylcyclopropane over a variety of metals and showed that the stereoselectivity of reaction varied with both metal solvent and acidity of the medium.[2]

RESULTS AND DISCUSSION

Our interests in the hydrogenolysis of the cyclopropane ring in substituted nortricyclenes arose because of the possible occurrence of this reaction as a step in the rearrangement of cycloalkanes over metal surfaces.[5] We thus studied the hydrogenolysis of 3-acetoxynortricyclene (1) with a view to obtaining knowledge on the stereochemistry of the reaction. The acetoxy-compound was chosen for this study as reaction with hydrogen over platinum in acetic acid containing a small amount of perchloric acid gave a predominance (68%) of 7-acetoxynorbornane (2). The n.m.r. spectrum of this latter compound had been reported previously in a study of the stereochemistry of hydrogenation of 7-acetoxynorbornadiene,[6] and could be used to assign the stereochemistry of deuterium incorporation into the molecule. In addition to the 7-acetoxy-compound (2) a smaller amount (32%) of the 2-*exo*-compound (3) was obtained. None of the 2-*endo*-isomer was detected (by g.l.c. or n.m.r.). The *endo*-compound only slowly isomerised to the *exo*-compound under the reaction conditions suggesting that the product ratio was kinetically controlled. The observed isomer ratio was in agreement with the relative ease of approach of the three edges of the cyclopropane ring to an assumed planar catalyst surface.

In order to study the stereochemistry of deuterium reaction with acetoxynortricyclene (1) it was necessary to differentiate between the *endo*- and *exo*- and *syn*- and *anti*-protons. Baird *et al.* have characterised the 60 MHz spectra by synthesis of a series of specifically labelled compounds. We repeated the synthesis of the stereospecifically labelled deuterium compounds as described by these workers and recorded their spectra at 220 MHz. The spectra were all of first order at high field and were assigned for 7-acetoxynorbornane as follows: δ 0.94 (*anti-endo*-H), 1.15 (*syn-endo*-H), 1.38 (*anti-exo*-H), 1.81 (*exo-syn*-H), 1.70 (OCOMe), 2.14 (1- and 4-H), and 4.88 (7-H) ($^2J_{exo\text{-}endo}$ 7.5 Hz). These assignments are in good agreement with those put forward by Baird and his co-workers.[6] Reaction of the acetoxy-compound (1) with deuterium over Adams catalyst at 80° for 72 h in acetic acid containing a drop of perchloric acid, gave a mixture of acetoxynorbornanes which were separated by preparative g.l.c. The predominant 7-acetoxy-compound (2) was collected and its ^{1}H n.m.r. spectrum recorded at 220 MHz. The absorptions at δ 0.94 and 1.15 now integrated for a single proton showing that deuterium incorporation was exclusively *cis-endo*. The data does not strictly differentiate between 2,5- and 2,6-di-*endo*-incorporation but the former would involve a highly improbable stereospecific rearrangement. Thus, the addition involves a stereospecific ($>95\%$) suprafacial *endo-cis*-addition of hydrogen to the 2,6-positions of the nortricyclene. The role of the perchloric acid in this reaction is not immediately obvious. Strong acids have been shown to lead to an increase in the proportion of antarafacial attack in other cyclopropane hydrogenolyses and proton transfer reactions have been proposed as steps in the hydrogenolysis.[2] This study suggests that if such



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[1] Preliminary communication: M. N. Akhtar, and W. R. Jackson, *J.C.S. Chem. Comm.*, 1972, 813.

[2] A. P. G. Kieboom, A. J. Breijer, and H. van Bekkum, *Rec. Trav. chim.*, 1974, **93**, 186.

[3] Z. Majerski and P. von R. Schleyer, *Tetrahedron Letters*, 1968, 6195.

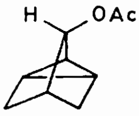
[4] U. R. Ghatak, P. C. Chakraborti, B. C. Ranu, and B. Sanyal, *J.C.S. Chem. Comm.*, 1973, 548.

[5] H. A. Quinn, M. A. McKervey, W. R. Jackson, and J. J. Rooney, *J. Amer. Chem. Soc.*, 1970 **92**, 2923.

[6] W. C. Baird, B. Franzus, and J. H. Surridge, *J. Org. Chem.*, 1969, **34**, 2944.

proton transfer reactions are involved they can still lead to overall suprafacial addition.

There has been much recent interest in the metal catalysed rearrangements of strained ring systems[7] since Hogeveen and Volger first reported the transition metal catalysed rearrangement of quadricyclene to norbornadiene.[8] In order to see whether hydrogenolysis of quadricyclenes could compete with such rearrangements the reaction of 7-acetoxyquadricyclene (4) with deuterium over platinum was investigated. The products from reaction of deuterium with either (4) or acetoxynorbornadiene (5) were found to have superimposable proton n.m.r. spectra at 220 MHz. In each case, the predominant isomer present was the *syn-endo*, *anti-exo*-isomer (6). Integration of the relevant absorptions showed that deuterium attack on (5) occurred: 10% *syn-exo*, 90% *syn-endo*, 25% *anti-endo*, and 75% *anti-exo*. These figures lie within the range suggested by Baird and his co-workers in their earlier study of the reaction of (5) with deuterium[6] and with the suggested preferred modes of attack for the *syn*- and *anti*-double bonds.[9] It thus appeared that the quadricyclene isomerises to the norbornadiene (5) faster than it reacts with hydrogen in the presence of a platinum catalyst. Further support for this view came from a hydrogenation which was stopped after *ca.* 10% uptake of hydrogen. Some of the acetoxyquadricyclene was shown by n.m.r. to have isomerised to norbornadiene in addition to that which was hydrogenated to 7-acetoxynorbornane.



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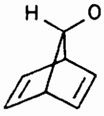

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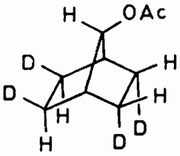

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EXPERIMENTAL

General.—M.p.s were determined with a Kofler hot stage apparatus and are corrected. I.r. spectra were recorded for liquid films or the KBr discs using a Perkin-Elmer Infracord 137 spectrometer. N.m.r. spectra were initially recorded for deuteriochloroform solutions by Mr. I. Jack using a Varian Associates A-60 spectrometer. Spectra of deuterium containing samples were recorded at 220 HMz by the National N.m.r. Centre, Harwell. Mass spectra were recorded using an A.E.I. MS 902 spectrometer. Analytical g.l.c. was carried out using a Perkin-Elmer F11 gas chromatograph fitted with a flame ionisation detector and a 2 m column of DEGS on Chromosorb W (20% of weight of support). Preparative g.l.c. involved a Wilkins Aerograph Autoprep (A-700) and a 20 m column of DEGS on Chromosorb P (30% of weight of support). Relative peak areas were measured using a Dupont 310 curve resolver and are accurate to ±2%.

Materials.—3-Acetoxynortricyclene had b.p. 84—87° at 13 mmHg, n_D^{24} 1.4680 (lit.,[10] 83—85° at 13 mmHg, n_D^{25} 1.4673—1.4681). 7-Acetoxynorbornadiene prepared from 7-t-butoxynorbornadiene by the method of Storey[11] had b.p. 76—78° at 18 mmHg, δ 6.71 (t, 2- and 3-*syn*-H), 6.58 (t, 5- and 6-*anti*-H), 4.60 (s, 7-H), 3.60 (m, 1- and 4-H), and 1.94 (s, $COCH_3$) (lit.,[11] b.p. 65° at 8 mmHg). 7-Acetoxyquadricyclene was prepared by photolysis of 7-acetoxynorbornadiene[12] and had m.p. 34—35° (lit.,[13] 34—35°). 2-*exo*-Acetoxynorbornane was prepared by addition of mercury(II) acetate to norbornene and had b.p. 80—84° at 7 mmHg, n_D^{22} 1.4571 (lit.,[14] n_D^{25} 1.4565). 2-*endo*-Acetoxynorbornane prepared by hydrogenation of 2-*endo*-acetoxynorbornene[15] had b.p. 86—88° at 17 mmHg (lit.,[16] 81—83° at 12 mmHg). 7-Acetoxynorbornane was prepared by hydrogenation of 7-acetoxynorbornadiene and purified by preparative g.l.c. at 75°.

Specifically Labelled Deuterio-compounds.—*syn*-2,3-Di-*exo*-deuterio-7-acetoxynorbornane,[17] *anti*-2,3-dideuterio-7-acetoxynorbornane,[18] and 2,3,5,6-tetra-*exo*-deuterio-7-acetoxynorbornane[18] were prepared by literature methods.

Hydrogenolysis of 3-Acetoxynortricyclene.—3-Acetoxynortricyclene (4 g) was hydrogenated in acetic acid (20 cm³) containing two drops of perchloric acid (70%) and Adams catalyst (0.2 g) at 80° for 72 h. The catalyst was removed by filtration and the product isolated in pentane. The solvent was removed through a column of glass helices to yield a mixture of acetoxynorbornanes (3.75 g, 93%). Analytical g.l.c. at 75° showed that 7-acetoxynorbornane (68%) and 2-*exo*-acetoxynorbornane (32%) were present. The *endo*-isomer could not be detected. Preparative g.l.c. at 110° gave samples of the two acetoxynorbornanes identical by i.r., n.m.r., and mass spectra with authentic samples.

A reaction of 3-acetoxynortricyclene (2.0 g) with deuterium was carried out under similar conditions in deuterioacetic acid (10 cm³) and gave deuterio-substituted acetoxynorbornanes (1.87 g, 93%) which were separated by preparative g.l.c.

Attempted Isomerisation of 2-endo-*Acetoxynorbornane.*—Adams catalyst (0.01 g) was added to a solution of 2-*endo*-acetoxynorbornane (0.2 g) in glacial acetic acid (3 cm³) and stirred under hydrogen at 80° for 24 h. Analytical g.l.c. and n.m.r. of the product showed that 2-*exo*-acetoxynorbornane (5%) was present together with the *endo*-isomer.

Reaction of 7-Acetoxynorbornadiene with Deuterium.—The diene (1.04 g) was stirred under deuterium at 20° for 4 h in deuterioacetic acid (10 cm³) in the presence of Adams catalyst (0.05 g). The product was isolated in pentane as a clear oil (1.0 g, 93%) shown to be 7-acetoxy-2,3-di-*endo*-

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[7] D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99; L. A. Paquette, *Accounts Chem. Res.*, 1971, **4**, 280.

[8] H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, 1967, **89**, 2486.

[9] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, 1970, **92**, 201.

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

[11] P. R. Storey, *J. Org. Chem.*, 1961, **26**, 287.

[12] G. S. Hammond, P. Wyatt, D. C. De Brer, and N. J. Turro, *J. Amer. Chem. Soc.*, 1964, **86**, 2532.

[13] H. G. Richey and N. C. Buckley, *J. Amer. Chem. Soc.*, 1963, **85**, 3057.

[14] S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, 1952, **74**, 1154.

[15] K. Alder and H. F. Rickert, *Annalen*, 1940, **543**, 1.

[16] R. L. Bixler and C. Niemann, *J. Org. Chem.*, 1958, **23**, 742.

[17] B. Franzus, W. C. Baird, and J. H. Surridge, *J. Org. Chem.*, 1968, **33**, 1288.

[18] B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, 1965, **87**, 3423.

5,6-di-*exo*-tetradeuterionorbornane by g.l.c. and spectroscopic methods, *m/e* 158 (M^+). Preparative g.l.c. at 110° gave an analytical sample (Found: C, 68.2; H + D, 11.6. Calc. for $C_9H_{10}D_4O_2$: C, 68.35; H + D, 12.1%).

Hydrogenolysis of 7-*Acetoxyquadricyclene*.—The acetate (0.2 g) was stirred over Adams catalyst (0.025 g) in acetic acid (2 cm^3) until absorption of hydrogen was complete (4 h). The product was isolated in pentane and analytical g.l.c. showed the presence of 7-acetoxynorbornane (92%) together with a small amount of 3-acetoxynortricyclene (8%).

A reaction was carried out with deuterium on a similar scale and the major products isolated by preparative g.l.c.

A small quantity of the quadricyclene (0.8 g) was stirred over freshly reduced Adams catalyst (80 mg) in acetic acid (5 cm^3) under nitrogen for 4 h. The product after isolation in pentane was shown to be starting material and 7-acetoxynorbornadiene in ratio *ca.* 4 : 1 by n.m.r.

In a further experiment, the quadricyclene (0.75 g) was stirred over Adams catalyst (0.1 g) in acetic acid (5 cm^3) under hydrogen until *ca.* 0.15 mole (20 cm^3) of hydrogen had been absorbed. The product (0.76 g) was isolated in pentane and shown by n.m.r. to consist of 7-acetoxyquadricyclene, 7-acetoxynorbornadiene, and 7-acetoxynorbornane in the ratio *ca.* 90 : 5 : 5.

We thank Johnson and Matthey Ltd. for a loan of platinum and the N.m.r. Service, Harwell, for 220 MHz spectra.

[5/1584 *Received*, 11*th August*, 1975]