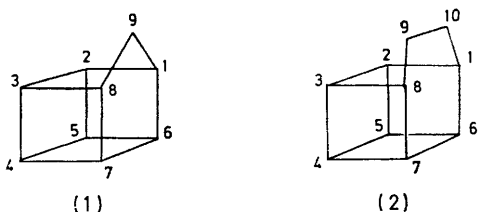


Preparation and Properties of Cage Polycyclic Systems. Part IV.¹ Hydrogenolyses of Homocubane Derivatives

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Hydrogenolyses and deuteriolyses of several homocubanes (pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonanes) in the presence of platinum-, palladium-, and rhodium-supported catalysts are described. 4-X-Homocubanes absorb 1 mol. equiv. of hydrogen to give 5-X-tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonanes by cleavage of the C(2)–C(5) bond. 9,9-Ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane, in the presence of rhodium–alumina (or rhodium–carbon), is hydrogenolysed by *endo,endo*-addition of hydrogen to give 3,3-ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane [by cleavage of the C(4)–C(5) bond] and 9,9-ethylenedioxytricyclo[4.3.0.0^{3,8}]nonane [by successive cleavages of the C(2)–C(5) and C(4)–C(7) bonds].

IN recent years, reactions of homocubane (1) and basketane (2) derivatives with metal ions, metal complexes in solution, and heterogeneous catalysts have been studied extensively, particularly those rearrangements promoted by rhodium(i) complexes² and by

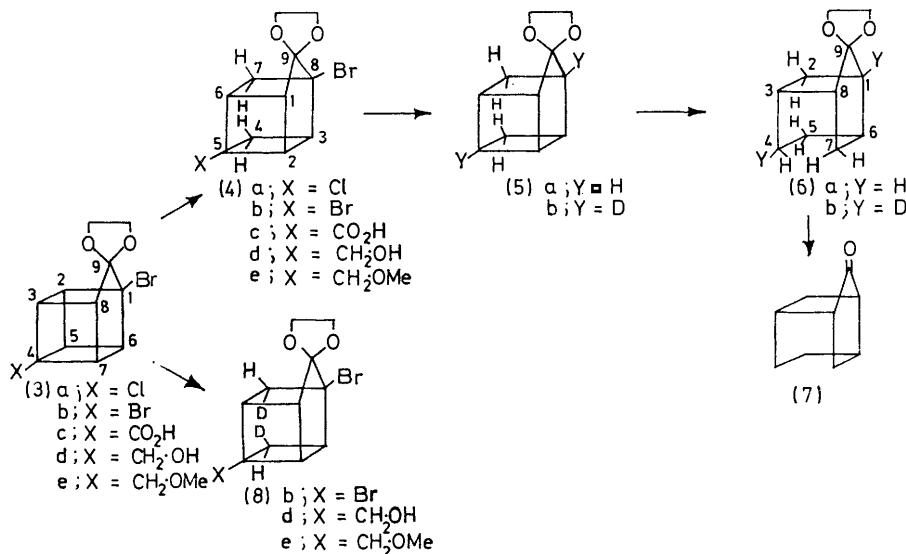


silver(i) ions.³ The hydrogenolysis of basketane derivatives over palladium catalysts has been reported,⁴ and Musso has shown that it is the C(2)–C(5) bond which is

cleaved by any of the catalysts mentioned above, nor in any of the following reactions: (i) base-induced homoallylic rearrangement of homocubanes;⁶ (ii) (a) base-induced homoketonisation of homocubane-4-ols,⁷ and (b) a similar base-induced cleavage of homocubyl ethers;⁸ and (iii) cationic cage-expansion reactions of homocubane-4-carbinols.⁹

We report here the results of hydrogenolysis and deuteriolysis of homocubanes in the presence of 5% platinum–carbon, 5 or 10% palladium–carbon, 5% rhodium–alumina, and 5% rhodium–carbon, including, we believe, the first example of cleavage of the C(4)–C(5) bond to give a novel tetracyclononane (12).

In 1968, we found¹⁰ that the hydrogenolysis of compound (3d) [and compound (3e)] with 10% palladium–



SCHEME

cleaved initially, not the C(4)–C(5) bond as had been suggested earlier.⁵ Indeed, the C(4)–C(5) bond in

¹ Part III, J. R. Bell, N. B. Chapman, and K. J. Toyne, *Tetrahedron*, 1975, **31**, 1683.

² L. A. Paquette, R. A. Boggs, and J. S. Ward, *J. Amer. Chem. Soc.*, 1975, **97**, 1118, and references quoted therein.

³ (a) L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *J. Amer. Chem. Soc.*, 1975, **97**, 1101; (b) L. A. Paquette, R. S. Beckley, and W. B. Farnham, *ibid.*, p. 1089; (c) L. A. Paquette and R. S. Beckley, *ibid.*, p. 1084.

⁴ (a) N. A. Sasaki, R. Zunker, and H. Musso, *Chem. Ber.*, 1973, **106**, 2992; (b) H. Musso, *ibid.*, 1975, **108**, 337.

carbon catalyst did not cleave the C(4)–C(5) bond and subsequently, by considering the effect of a shift reagent

⁵ S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Letters*, 1966, 1017.

⁶ A. J. H. Klunder and B. Zwanenburg, *Tetrahedron*, 1975, **31**, 1419.

⁷ A. J. H. Klunder and B. Zwanenburg, *Tetrahedron*, 1973, **29**, 1683.

⁸ R. D. Miller and D. L. Dolce, *Tetrahedron Letters*, 1973, 5217.

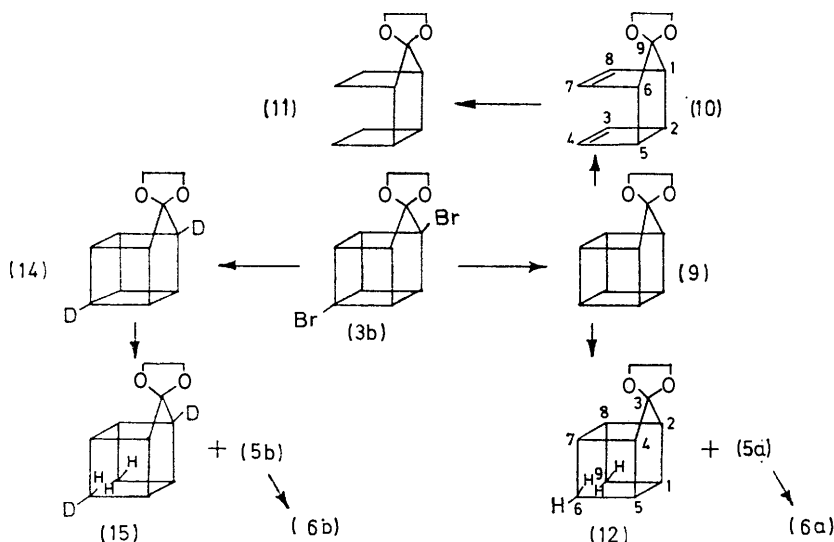
⁹ A. J. H. Klunder and B. Zwanenburg, *Tetrahedron*, 1973, **29**, 161.

¹⁰ J. M. Key, Ph.D. Thesis, 1968, University of Hull.

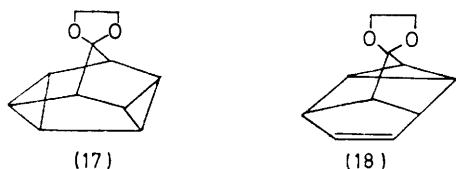
on the n.m.r. spectrum of the hydrogenolysis product showed that the C(2)-C(5) bond was broken.¹¹ We have now found that the C(2)-C(5) bond in compounds (3a-c) is also hydrogenolysed over platinum-carbon, palladium-carbon, or rhodium-alumina, and that hydrogenolysis to a tetrahydro-derivative is insignificant. For all these compounds, the presence of the 4-substituent may be responsible both for preventing cleavage of the C(4)-C(5) bond and for preventing formation of a tetrahydro-derivative.

We have therefore studied the hydrogenolysis of compounds (9) and (14) in the presence of these catalysts to find out the mode of cleavage in the absence of a 4-substituent. With 5% platinum-carbon and with 5 or 10% palladium-carbon a large number of products

gives only two primary products [compounds (12) and (5a) are formed after 2 h], and after prolonged hydrogenolysis (1-2 days) compound (5a) is converted into compound (6a). Secondly, the formation of compound (12) is, we believe, the first example of cleavage of the C(4)-C(5) bond, and the amounts of compounds (12) and (6a) formed indicate that a C(4)-C(5) bond is cleaved about four times as readily as a C(2)-C(5) bond. The structure of compound (12) is confirmed by the following evidence: mass (M^+ 178) and ¹H n.m.r. spectroscopy indicate a dihydro-product, i.e. spectroscopy (absence of absorptions above 3000 cm⁻¹) excludes a cyclopropane ring, and ¹³C n.m.r. spectroscopy indicates only five types of carbon atom. The structure of compound (6a) is similarly confirmed by its non-identity with



were formed from compound (9) and isolation of these was not attempted. Platinum-carbon gave at least 8 products, including compounds (5a) and (6a) (identified by g.l.c.), and palladium-carbon gave at least 10 products, including compound (5a) (identified by g.l.c.) but neither catalyst gave any cleavage of the C(4)-C(5) bond. This fact is confirmed by hydrogenolysing compound (12) (prepared as described below) over platinum or palladium to give products (as detected by g.l.c.) distinct from the hydrogenolysis products of compound (9). The large number of compounds formed with platinum or palladium as catalyst probably include rearrangement products such as (17) and (18), and their hydrogenation or hydrogenolysis products.^{2,4}



The reaction of compound (9) with 5% rhodium-alumina is markedly different in two respects from the reactions with the other catalysts. First, the reaction

another possible tetrahydro-product (11), by spectral evidence, and by its hydrolysis to the known compound (7). Compound (5a) is more conveniently prepared from compound (3a, b, or c) by the sequence shown in the Scheme, and its subsequent conversion into compound (7) confirms that the initial hydrogenolyses of compounds (3a-c) break the C(2)-C(5) bond.

The stereochemistry of the hydrogenolyses in these ring systems is believed to be such that the addition of hydrogen atoms occurs mainly, if not entirely, in an *endo,endo*-fashion. Integration of the n.m.r. spectrum of compound (15) gives a ratio of methylene cage protons of 2:1, which indicates that the hydrogen atoms have been added *endo,endo* or *exo,exo*. *endo*-Protons would be expected to suffer van der Waals deshielding and, on this assumption, the observation of a one-proton signal at δ 1.90-2.11 and signals for two protons at 2.22-2.29 (in CDCl₃) is in keeping with *endo,endo*-addition.

Musso^{4a} has suggested that the sequence in which bond cleavage occurs in hydrogenolysis of strained polycyclic compounds depends, *inter alia*, on (a) the C-C bond lengths, (b) the angle strain relieved by bond

¹¹ K. J. Toyne, unpublished work.

cleavage, and (c) the interaction of the compound with the catalyst surface, and he invoked a combination of the first two factors to explain the bond cleavages in basketanes. For homocubanes the lengths of the C(2)–C(5) and C(4)–C(5) bonds are approximately the same (1.55 Å),¹² but cleavage of the C(2)–C(5) bond probably gives greater relief of cage strain than is achieved by cleavage of the C(4)–C(5) bond,⁹ and therefore factor (c) or other factors are necessary to explain cleavage of the C(4)–C(5) bond by rhodium–alumina. One possible factor is the nature of the catalyst support. There is evidence that in some reactions the reactivity of the catalyst depends on the particle (crystallite) size,¹³ which is in turn dependent on the nature of the support. We have therefore hydrogenolysed compound (9) in the presence of 5% rhodium–carbon in cyclohexane. Qualitatively the reaction was similar to that with rhodium–alumina but the product (as determined by g.l.c.) contained 73% of compound (6a) and 27% of compound (12), whereas with alumina as support in the same solvent the percentages were 45 and 55, respectively.

Further study of the hydrogenolysis of basketanes, homocubanes, and other strained ring systems is necessary to establish whether or not the crystallite size of the catalyst is an important factor.

EXPERIMENTAL

I.r. spectra were recorded by using a Perkin-Elmer 457 spectrophotometer. N.m.r. spectra were recorded at 100 MHz with a JEOL 4H-100 spectrometer, with tetramethylsilane as internal standard and CDCl₃ as solvent. Mass spectra were recorded with an A.E.I. MS902 spectrometer; *m/e* values are given for bromine-79 and chlorine-35. G.l.c. analyses, unless otherwise stated, were carried out with a Perkin-Elmer F11 instrument fitted with a glass column (2.0 m × 3 mm i.d.) packed with 20% silicone gum rubber (SE-301) on Chromosorb W, at a column temperature of 180 °C. The combustion analyses of deuterium compounds were not obtained; all other compounds gave satisfactory analyses* for carbon and hydrogen, and for bromine and chlorine when present. The catalysts were obtained from the Engelhard Chemical Group (rhodium and palladium) and from Johnson, Matthey and Co. Ltd. (platinum).

1-Bromo-4-chloro-9,9-ethylenedioxy-pentacyclo[4.3.0.0^{2,5}.-0^{3,8}.0^{4,7}]nonane (3a)¹⁰ was prepared by chlorodecarboxylation of compound (3c)¹⁴ by Kochi's method.¹⁵ The product was eluted from a silica gel column (30 × 2 cm) with carbon tetrachloride; yield 59%; m.p. 120–123° (from ethanol); ν_{\max} (KCl) 3 035, 3 000, 2 910, 1 300, 761, and 662 cm⁻¹; δ 2.99–3.15 (1 H, m), 3.52–3.79 (5 H, m), and 3.82–4.30 (4 H, sym. m); *m/e* 288 (*M*⁺), 209, 165, 102, and 101.

1-Bromo-9,9-ethylenedioxy-4-(methoxymethyl)pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (3e) was prepared (78%) from

* Available as Supplementary Publication No. SUP 21745 (2 pp.); for details of Supplementary Publications see Notice to Authors No. 7 (*J.C.S. Perkin I*, 1975, Index Issue).

¹² W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *J. Amer. Chem. Soc.*, 1971, **93**, 1446.

¹³ T. E. Whyte, in 'Catalysis Reviews,' vol. 8, ed. H. Heinemann, Dekker, New York, 1974, p. 117.

compound (3d)^{9,10} by treatment, successively, with sodium hydride and methyl iodide in 1,2-dimethoxyethane, and had m.p. 98–100° (from ethanol); ν_{\max} (KCl) 3 027, 3 010, 2 992, 2 937, 2 900, 2 860, 2 836, 1 477, 1 305, and 1 158 cm⁻¹; δ (CCl₄) 2.76–2.91 (1 H, m), 3.36–3.53 (7 H, m, with s at 3.41), 3.32 (3 H, s), and 3.87–4.31 (4 H, sym. m); *m/e* 298 (*M*⁺), 187, 115, 112, and 77.

Hydrogenolysis or Deuteriolysis of Compounds (3a–e).—Unless otherwise stated, the compounds were hydrogenolysed (a) or deuteriolysed (b) in AnalaR glacial acetic acid or glacial acetic [²H]acid over 10% palladium–carbon until the theoretical volume of hydrogen or deuterium had been absorbed (*ca.* 1 h). The product was obtained by filtration and evaporation.

Compound (3a) gave (a) 8-bromo-5-chloro-9,9-ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (4a) (86%), m.p. 73–75° (from glacial acetic acid–water, 1:1); ν_{\max} (KCl) 2 990, 2 900, 1 310, 1 290, 1 157, 1 033, 923, 682, 517, and 448 cm⁻¹; δ 2.23–2.39 (1 H, q), 2.42–2.54 (3 H, m), 2.60–2.68 (1 H, q), 2.73–2.85 (1 H, m), 3.00–3.12 (1 H, t), 3.25–3.35 (1 H, m), and 3.80–4.30 (4 H, m); *m/e* 290 (*M*⁺), 255, 211, 132, and 103.

Compound (3b)^{10,16} gave (a) 5,8-dibromo-9,9-ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (4b) (77%) with either 10% palladium–carbon in AnalaR methanol or 5% rhodium–alumina in AnalaR methanol; m.p. 96–98° (from ethanol); ν_{\max} (KCl) 2 985, 2 900, 1 305, 1 288, 1 152, 1 073, 917, 682, 514, and 417 cm⁻¹; δ 2.41–2.76 (5 H, m), 2.86–3.06 (1 H, m), 3.16 (1 H, t), 3.36–3.53 (1 H, sextet), and 3.86–4.36 (4 H, m); and (b) 5,8-dibromo-endo,endo-4,7-dideuterio-9,9-ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (8b) (65%) with 10% palladium–carbon in methan[²H]ol; m.p. 97–99° (from methanol–water); ν_{\max} (KCl) 2 985, 2 900, 2 205, 1 293, 1 159, and 1 030 cm⁻¹; δ 2.50–2.64 (2 H, m), 2.64–2.79 (1 H, m), 2.85–3.03 (1 H, m), 3.03–3.27 (1 H, m), 3.33–3.54 (1 H, sextet), and 3.84–4.38 (4 H, m).

Compound (4b) was also prepared from compound (4c) by a modification of the Hunsdiecker reaction.¹⁷

Compound (3c)¹⁴ gave (a) 8-bromo-9,9-ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane-5-carboxylic acid (4c) (75%), m.p. 180–183° (from glacial acetic acid–water 1:1); ν_{\max} (KCl) 3 500–2 500, 2 985, 2 886, 1 685, 1 304, 1 289, 1 095, and 1 038 cm⁻¹; δ 2.16–2.66 (5 H, m), 2.84–3.07 (2 H, m), 3.22–3.38 (1 H, sextet), 3.84–4.36 (4 H, m), and 10.41br (1 H); *m/e* 300 (*M*⁺), 221, 131, 105, and 103.

Compound (3d)^{9,10} gave (a) 8-bromo-9,9-ethylenedioxy-5-(hydroxymethyl)tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (4d) (80%), m.p. 40–42° (from water–ethanol, 10:1); ν_{\max} (KCl) 3 600–3 100br, 2 978, 2 890, 1 300, 1 288, 1 153, and 1 033 cm⁻¹; δ 1.95–2.05 (3 H, m; includes OH), 2.37–2.48 (4 H, m), 2.78–3.05 (2 H, m), 3.55 (2 H, s), and 3.83–4.35 (4 H, m); *m/e* 286 (*M*⁺), 268, 175, 131, and 103; and (b) 8-bromo-endo,endo-4,7-dideuterio-9,9-ethylenedioxy-5-(hydroxymethyl)tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (8d), m.p. 40–42°; δ 1.93–2.03 (2 H, m; includes OH), 2.35–2.50 (3 H, m), 2.80–3.05 (2 H, m), 3.53 (2 H, s), and 3.80–4.33 (4 H, m); *m/e* 288 (*M*⁺), 270, 176, 131, and 64.

Compound (3e) gave (a) 8-bromo-9,9-ethylenedioxy-5-

¹⁴ N. B. Chapman, J. M. Key, and K. J. Toyne, *J. Org. Chem.*, 1970, **35**, 3860.

¹⁵ J. K. Kochi, *J. Amer. Chem. Soc.*, 1965, **87**, 2500.

¹⁶ A. J. H. Klunder and B. Zwanenburg, *Tetrahedron*, 1972, **28**, 4131.

¹⁷ S. J. Cristol and W. C. Firth, *J. Org. Chem.*, 1961, **26**, 280.

(methoxymethyl)tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (4e) (90%), m.p. 60–61° (from ethanol); ν_{\max} (KCl) 3 004, 2 997, 2 980, 2 915, 2 846, 2 830, 1 480, 1 295, and 1 040 cm^{-1} ; δ 1.95–2.09 (2 H, m), 2.23–2.54 (4 H, m), 2.75–2.99 (2 H, m), 3.31 (2 H, s), 3.33 (3 H, s), and 3.80–4.41 (4 H, m); m/e 300 (M^+), 255, 221, 102, and 99; and (b) 8-bromo-endo,endo-4,7-dideuterio-9,9-ethylenedioxy-5-(methoxymethyl)tetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (8e), m.p. 60–61°; ν_{\max} (KCl) 2 972, 2 900, 2 820, 2 180, 1 290, 1 159, 1 100, and 1 032 cm^{-1} ; δ 1.87–2.09 (1 H, m), 2.23–2.61 (3 H, m), 2.73–2.99 (2 H, m), 3.31 (2 H, s), 3.33 (3 H, s), and 3.82–4.44 (4 H, m); m/e 302 (M^+), 257, 223, 99, and 83.

9,9-Ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (5a) was prepared (60%) from compound (4a) or (4b) by using lithium-*t*-butyl alcohol-tetrahydrofuran,¹⁸ and had b.p. 110° at 14 mmHg; ν_{\max} (film) 2 960, 2 870, 1 325, 1 130, and 1 085 cm^{-1} ; δ 1.73–2.06 (4 H, m), 2.06–2.18 (1 H, m), 2.37–2.52 (1 H, m), 2.52–2.75 (3 H, m), 2.85–3.05 (1 H, m), and 3.81–3.95 (4 H, m); m/e 178 (M^+), 177, 99, 91, and 55. 5,8-Dideuterio-9,9-ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonane (5b) was prepared from compound (4a) by using lithium-*t*-butyl [²H]alcohol-tetrahydrofuran (cf. ref. 18); ν_{\max} (film) 2 960, 2 875, 2 205, 1 310, 1 294, and 1 045 cm^{-1} ; δ 1.74–2.08 (4 H, m), 2.39–2.54 (1 H, q), 2.54–2.80 (2 H, m), 2.87–3.07 (1 H, m), and 3.82–4.00 (4 H, m).

9,9-Ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (9) was prepared (73%) from compound (3b)^{10,16} by using lithium-*t*-butyl alcohol-tetrahydrofuran in a method similar to that described by Bruck;¹⁸ b.p. 95–98° at 3 mmHg (lit.,¹⁰ 180–182° at 30 mmHg; lit.,¹⁹ 85–87° at 3 mmHg); ν_{\max} (film) 2 980, 2 880, 1 190, 1 060, and 1 010 cm^{-1} ; δ 2.86–3.06 (2 H, m), 3.14–3.36 (2 H, m), 3.42–3.64 (4 H, m), and 3.93 (4 H, s); m/e 176 (M^+), 175, 104, 103, and 78.

9,9-Ethylenedioxytricyclo[4.2.1.0^{2,5}]nona-3,7-diene (10).—Compound (9) (0.50 g) and norbornadienerhodium chloride²⁰ [(Rh(nor)Cl)₂] (0.01 g) in dry AnalaR benzene (20 ml) were stirred at room temperature for 3 weeks. The mixture was diluted with ether, washed with aqueous sodium cyanide and water, and dried (MgSO₄). The solvents were removed by distillation to give compound (10) (0.45 g, 90%), b.p. 95–96° at 4 mmHg; ν_{\max} (film) 3 105, 3 035, 2 970, 2 880, 1 285, 1 142, 1 071, 787, 701, and 519 cm^{-1} ; δ 2.47–2.60 (2 H, m), 3.09–3.20 (2 H, m), 3.74–3.96 (4 H, m), 5.77 (2 H, s), and 5.93–5.99 (2 H, t); m/e 176 (M^+), 175, 149, 131, and 104.

9,9-Ethylenedioxytricyclo[4.2.1.0^{2,5}]nonane (11) was prepared (80%) by hydrogenating compound (10) over 7.5% palladium-carbon in cyclohexane; b.p. 85–87° at 3 mmHg; ν_{\max} (film) 2 955, 2 875, 1 322, 1 168, 1 070, and 730 cm^{-1} ; δ 1.65–1.77 (2 H, m), 1.79–1.93 (4 H, m), 1.94–2.12 (4 H, m), 2.67–2.97 (2 H, m), and 3.89 (4 H, s); m/e 180 (M^+), 151, 99, 80, and 79.

1,4-Dideuterio-9,9-ethylenedioxytetracyclo[4.3.0.0^{2,5}.-

0^{3,8}.0^{4,7}]nonane (14) was prepared (70%) from compound (3b)^{10,16} by the method used for preparing compound (9), but with *t*-butyl [²H]alcohol; b.p. 98–100° at 3 mmHg; ν_{\max} (film) 2 975, 2 875, 2 245, 1 304, 1 183, 1 055, and 511 cm^{-1} ; δ 2.87–3.02 (1 H, m), 3.17–3.32 (1 H, m), 3.46–3.56 (4 H, t), and 3.90 (4 H, s).

Hydrogenolysis of Compounds (9) and (14) over Rhodium-Alumina.—(A) Compound (9) (1.0231 g) in cyclohexane (20 ml) was hydrogenolysed at atmospheric pressure and room temperature with 5% rhodium-alumina (0.25 g). After 24 h more catalyst (0.25 g) was added and the hydrogenation was complete after 48 h. The catalyst was filtered off and the filtrate was concentrated by distillation. Preparative g.l.c. [glass column (3 m × 7 mm i.d.); 10% Carbowax 20M on Chromosorb W at 150 °C] gave two fractions: (i) 9,9-ethylenedioxytricyclo[4.3.0.0^{3,8}]nonane (6a) (0.3826 g, 37%); ν_{\max} (film) 2 945, 2 868, 1 319, 1 220, 1 191, 1 110, and 1 063 cm^{-1} ; δ_{H} 1.22–1.72 (6 H, m), 1.72–2.10 (6 H, m), and 3.89 (4 H, s); $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 1.23–1.33 (2 H, q), 1.40–1.74 (4 H, m), 1.82–2.12 (4 H, m), 2.16–2.42 (2 H, m), and 3.52 (4 H, s); δ_{C} (proton-decoupled) 24.76, 29.96, 30.09, 42.44, and 64.21 (absorption for C-9 not observed); m/e 180 (M^+), 137, 99, 80, and 79; and (ii) 3,3-ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{4,7}]nonane (12) (0.4129 g, 40%); ν_{\max} (film) 2 960, 2 880, 1 367, 1 118, and 1 016 cm^{-1} ; δ_{H} 1.86–2.08 (2 H, m), 2.16–2.29 (2 H, d), 2.52–2.70 (6 H, m), and 3.90 (4 H, s); $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 1.74–1.96 (2 H, m), 2.09–2.17 (2 H, d), 2.54–2.73 (6 H, m), and 3.58 (4 H, s); δ_{C} (proton-decoupled) 27.43, 37.89, 56.80, 64.99, and 115.94; m/e 178 (M^+), 137, 112, 91, and 68.

Compound (6a) (b.p. 101–103° at 5 mmHg) was also prepared by hydrogenolysis of compound (5a) with 5% rhodium-alumina in cyclohexane. Compound (6a) was hydrolysed with concentrated hydrochloric acid in tetrahydrofuran to give material identical (i.r. and n.m.r. spectra) with tricyclo[4.3.0.0^{3,8}]nonan-9-one (7).²¹

(B) Compound (14) was hydrogenolysed by a similar procedure to produce two fractions (by g.l.c.): (i) 1,4-dideuterio-9,9-ethylenedioxytricyclo[4.3.0.0^{3,8}]nonane (6b); ν_{\max} (film) 2 950, 2 870, 2 170, 1 296, 1 219, and 1 045 cm^{-1} ; δ 1.19–1.79 (5 H, m), 1.79–2.11 (5 H, m), and 3.87 (4 H, s); $\delta(\text{C}_6\text{D}_6)$ 1.22–1.32 (2 H, d), 1.45–1.72 (3 H, m), 1.80–2.08 (3 H, m), 2.13–2.37 (2 H, m), and 3.52 (4 H, s); and (ii) 2,exo-6-dideuterio-3,3-ethylenedioxytetracyclo[4.3.0.0^{2,5}.0^{4,7}]nonane (15); ν_{\max} (film) 2 960, 2 885, 2 175, 1 349, 1 079, and 1 040 cm^{-1} ; δ 1.90–2.11 (1 H, m), 2.22–2.29 (2 H, d), 2.57–2.72 (5 H, m), and 3.90 (4 H, s); $\delta(\text{C}_6\text{D}_6)$ 1.75–1.97 (1 H, m), 2.08–2.18 (2 H, m), 2.55–2.70 (5 H, m), and 3.58 (4 H, s).

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[5/2291 Received, 24th November, 1975]

¹⁸ P. Bruck, *Tetrahedron Letters*, 1962, 449.

¹⁹ B.P. 1,068,655 (*Chem. Abs.*, 1968, 68, 2640).

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