Synthesis and Acid-catalysed Rearrangement of (1R,2R,5S,6S)-Tricyclo-[4.3.1.1²,⁵]undecane

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(1R,2R,5S,6S)-Tricyclo[4.3.1.1²,⁵]undecane (II) was synthesised by hydride transfer reduction–ring expansion of (1RS,2RS,6RS,7SR)-2-hydroxymethyltricyclo[5.2.1.0²,⁶]decane (I) with sulphuric acid and n-pentane. The (1RS,2SR,6SR,7SR)-isomer (VIII) of (I) did not undergo ring expansion, but gave a simple reduction product, i.e. the 2-methyl derivative (X). Further isomerisation of the tricycloundecane (II) gave (1RS,2RS,6SR,7SR)-2-methyltricyclo[5.2.1.0²,⁶]decane (X) and its (1RS,2SR,6RS,7SR)-isomer, (XI), tricyclo[5.3.1.0³,⁸]undecane (XII), tricyclo[5.3.1.0²,⁶]undecane (V), and 2-methyladamantane. The 2-methyltricyclodecanes (X) and (XI) were isomerised quantitatively to methyladamantanes in the presence of aluminium chloride.

HYDRIDE transfer reduction–rearrangement of carbinols and olefins has been proved to be a useful method of preparing polycyclic hydrocarbons.[1] The reaction has now been applied to the 2-hydroxymethyltricyclo[5.2.1.0²,⁶]-decane (I) to give (1R,2R,5S,6S)-tricyclo[4.3.1.1²,⁵]un-decane (II).

The carbinol (I), prepared by reduction (lithium aluminium hydride) of the methyl ester (III) of the corresponding carboxylic acid (IV),[2] was stirred with 95% sulphuric acid and n-pentane for 10 min at room temperature. Evaporation of the pentane layer followed by preparative g.l.c. gave a new tricycloundecane, comprising 91% of the product mixture. Whereas no conclusive evidence about the structure was obtained from the i.r., ¹H n.m.r., and mass spectra of the compound, the ¹³C n.m.r. spectrum was very informative. The presence of seven different kinds of carbon atom was indicated, consisting of four pairs and three single atoms. All three single carbon atoms exhibited triplet absorption (CH₂) in the off-resonance proton-decoupled spectrum. No methyl group (quartet) was detected.

Of the possible 70 tricycloundecanes containing neither three- nor four-membered rings,[3] only four structures are consistent with the ¹³C n.m.r. data: (II)

|	R			R	
(I)	CH₂·OH		(VIII)	CH₂·OH	
(III)	CH₂Me		(IX)	CO₂H	
(IV)	CO₂H		(X)	Me	
(XI)	Me				
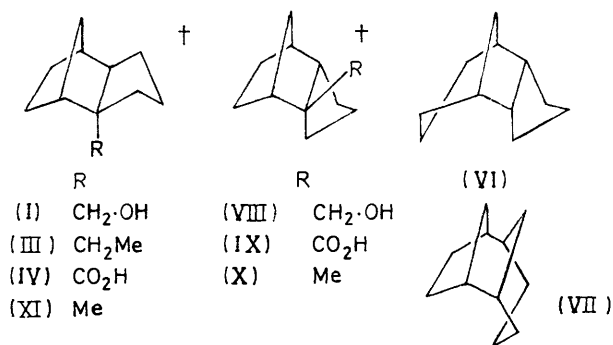
† Compounds (I), (III), (IV), and (VIII)—(XI) are all racemic mixtures; only one enantiomer is illustrated.

and (V)—(VII). However compounds (V) and (VI) had been previously prepared by us[3] and were different from the new tricycloundecane; thus a choice between structures (II) and (VII) was required. The former was preferred on the basis of the well documented ring expansion

[1] (a) Z. Majerski and K. Mlinaric, J.C.S. Chem. Comm., 1972, 1030; (b) K. M. Majerski and Z. Majerski, Tetrahedron Letters, 1973, 4915; (c) J. Janjatovic, D. Skare, and Z. Majerski, J. Org. Chem., 1974, **39**, 651; (d) J. S. Wishnok, P. von R. Schleyer, E. Funke, G. D. Pandit, R. O. Williams, and A. Nikon, ibid., 1973, **38**, 539.

[2] H. Koch and W. Haaf, Annalen, 1960, **638**, 111.

[3] N. Takaishi, Y. Inamoto, K. Aigami, and E. Ōsawa, J. Org. Chem., in the press.

of *endo*-norbornan-2-ylmethyl and bicyclo[4.3.0]nonan-1-ylmethyl systems,[4] as well as the reactivity of the 2-hydroxymethyltricyclo[5.2.1.0^{2,6}]decane (VIII) which, as
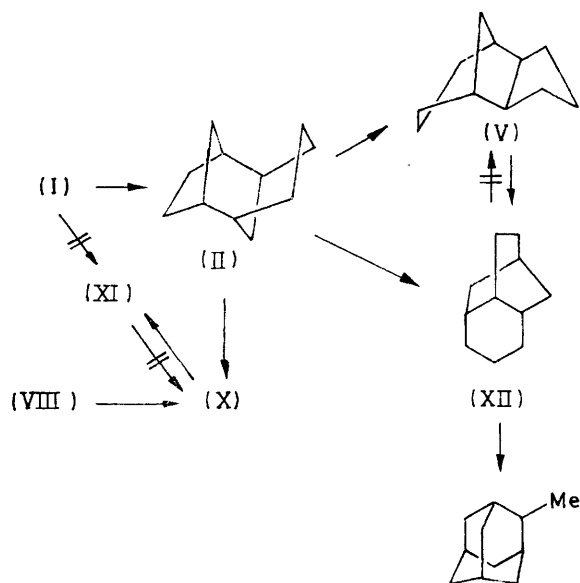
described below, was in strong contrast to that of its stereoisomer (I).

The carbinol (VIII), prepared like (I) from the corresponding carboxylic acid (IX),[2] did not give the ring expansion product (VII) when treated with sulphuric acid and n-pentane: the reaction merely resulted in reduction of the hydroxymethyl to a methyl group without any skeletal rearrangement. The product (X) (93% of the total products) was identified by comparison with an authentic specimen prepared by reduction (lithium aluminium hydride) of the tosylate [5] of the carbinol (VIII).

Among the by-products of the hydride transfer reduction of (I) were the methyl derivative (X), the tricyclo[5.3.1.0^{2,6}]undecane (V),[3] and tricyclo[5.3.1.0^{3,8}]undecane (XII).[1b,3,6-8] In order to discover whether these compounds were formed directly from (I), the further isomerisation of (II) by sulphuric acid at ambient temperature was studied. Under these conditions compound (II) was partly converted into a mixture mainly consisting of (V), (X), (XI), (XII), and 2-methyladamantane. Interconversion between two isomeric methyltricyclo[5.2.1.0^{2,6}]decanes (X) and (XI) was examined separately in sulphuric acid as well as in the presence of aluminium chloride. Although the isomerisation (X) ⟶ (XI) was fairly slow in sulphuric acid, the reaction was effectively

catalysed by aluminium chloride, and was almost complete before any significant amount of methyladamantane was observed. Thus the equilibrium between (X) and (XI) was shown to be greatly in favour of the latter. Compounds (X) and (XI) were ultimately isomerised to methyladamantane almost quantitatively.

DISCUSSION

The fact that the carbinol (VIII) did not undergo ring expansion is unexpected in view of the behaviour of its isomer (I), as well as of the reported expansion of cyclopentylmethyl to cyclohexyl systems in simpler bridged molecules.[4] Acetolysis of norbornan-2-yl tosylates, for example, gave bicyclo[3.2.1]octyl acetates in 75—85% yield with over 90% selectivity in favour of the 2-yl acetate, from either of the epimeric tosylates.[4d] This result indicates predominant migration of the 2,3-bond rather than the 1,2-bond on ring expansion, irrespective of the conformation of the carbinyl group. Ring expansion of (VIII) would be expected to give the tricyclo[4.3.1.1^{2,5}]undecane (VII) if the same stereoelectronic requirement as in norbornylmethyl ring expansion was the only controlling factor. The suppression of ring expansion is considered to be attributable to the instability of the product (VII) arising from accumulated non-bonded repulsions.* Consequently, of the two alternative reaction pathways of the cation from (VIII), the process of hydride transfer leading to (X) may involve a relatively low activation energy, as compared to the high energy of (VII) and hence of its bridgehead(1-position) cation, which could be approximated to the transition state for the ring expansion.

Formation of the methyltricyclodecane (X) in the sulphuric acid-catalysed rearrangement of (II) could be explained by the intermediacy of (VII), formed in turn by a Wagner–Meerwein rearrangement of (II). Extrusion of a methyl group from (VII), releasing a part of the conformational energy, would give rise to (X). The presence of a small amount of (XI) could be a result of a Wagner–Meerwein rearrangement of (X), which is relatively slow in sulphuric acid. An alternative route leading to (X), involving extrusion of a methyl group from (II) to form (XI) which then rearranges to (X), is clearly excluded by the experiment on the interconversion of (X) and (XI).

Tricyclo[5.3.1.0^{3,8}]undecane (XII), also formed in the rearrangement of (II), is obtainable from several other precursors under a variety of reaction conditions,[1b,3,7,8,10] and appears to be one of the most stable tricycloundecane isomers. Compound (V) must be formed directly from

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* Structure (VII) should have an appreciable excess of energy over the isomer(II), in view of the difference (9·7 kcal mol^{-1}) in estimated standard heats of formation of the two tricyclo[4.2.1.1^{2,5}]decanes,[9] which are the lower homologues of (II) and (VII).

[4] (a) J. A. Berson and R. Reynolds-Warnhoff, *J. Amer. Chem. Soc.*, 1962, **84**, 682; (b) J. A. Berson and D. Willner, *ibid.*, p. 675; (c) M. A. McKinney and P. P. Patel, *J. Org. Chem.*, 1973, **38**, 4059; (d) R. R. Sauers and R. T. Tucker, *ibid.*, 1963, **28**, 876; (e) P. K. Freeman and K. B. Desai, *ibid.*, 1971, **36**, 1554; (f) C. D. Gutsche and D. Redmore, 'Carbocyclic Ring Expansion Reactions,' Academic Press, New York, 1968, p. 3.

[5] H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, 1959, **92**, 1629.
[6] A. Krantz and C. Y. Lin, *Chem. Comm.*, 1971, 1287; *J. Amer. Chem. Soc.*, 1973, **95**, 5662.
[7] N. Takaishi, Y. Inamoto, and K. Aigami, *Chem. Letters*, 1973, 1185.
[8] M. Farcaşiu, K. R. Blanchard, E. M. Engler, and P. von R. Schleyer, *Chem. Letters*, 1973, 1189.
[9] E. M. Engler, M. Farcaşiu, A. Sevin, J. M. Cense, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5769.
[10] N. Takaishi, Y. Inamoto, and K. Aigami, unpublished work.

(II) rather than from (XII) because the latter has been shown [10] not to isomerise to (V) in sulphuric acid. Compound (V) as well as (XII) can also arise directly from (I): hydride transfer reduction of (I) for 10 min gave small amounts of (V) and (XII), whereas almost no change was detected after treatment of (II) with sulphuric acid for 1 h.

None of the tricycloundecanes (II), (V), and (XII) were obtained in the isomerisation of the methyltricyclodecanes (X) and (XI), indicating that the methyl group, once formed, is not incorporated back into ring system. Formation of methyladamantanes from (X) and (XI), therefore, cannot involve the intermediacy of these tricycloundecanes, but must occur by rearrangement of the tricyclodecane skeleton alone, leaving the methyl group intact. This is also the case in the interconversion of 1- and 2-methyladamantane.[11]

EXPERIMENTAL

I.r. spectra were obtained for neat samples with a Hitachi 215 spectrophotometer. ^{1}H N.m.r. spectra were measured with a Varian T-60 instrument (deuteriochloroform as solvent and tetramethylsilane as internal standard), and ^{13}C n.m.r. spectra were obtained at 20 MHz with a Varian CFT-20 spectrometer. Mass spectra were measured with a Hitachi RMU-6D spectrometer (75 eV ionisation voltage). G.l.c. was carried out with a Shimazu GC-4B-PTF chromatograph and columns (1/4 in × 6 ft) packed with 60—80 mesh Chromosorb W containing 30% of silicone SE-30, Carbowax 20M, Apiezon L, or DEGS. G.l.c.–mass spectrometry was performed with a JEOL JGC-20-KP instrument [columns (0·01 in × 150 ft) packed with Apiezon L or silicone SE-30] connected to a JEOL JMS-D100 mass spectrometer. Preparative g.l.c. was carried out with a Varian Aerograph 700 instrument.

A mixture of the tricyclo[5.2.1.0^{2,6}]decane-2-carboxylic acids (IV) and (IX), obtained by Koch carboxylation of tricyclo[5.2.1.0^{2,6}]decan-8-ol was converted into methyl esters via the acid chlorides.[2] The mixture of esters [62% (III) and 38% methyl ester of (IX)] was separated by fractional distillation through a 2 ft Vigreux column and the esters were purified by preparative g.l.c. Methyl (1RS,2RS,6RS,-7SR)-tricyclo[5.2.1.0^{2,6}]decane-2-carboxylate (III) had b.p. 78—80° at 2 mmHg (Found: C, 72·85; H, 9·4. Calc. for C$_{12}$H$_{16}$O$_2$: C, 74·2; H, 9·35%), $n_D^{26·2}$ 1·4857 (lit.,[2] n_D^{20} 1·4883); and the (1RS,2SR,6SR,7SR)-isomer had b.p. 87—89° at 2 mmHg (Found: C, 74·0; H, 9·5%), $n_D^{26·5}$ 1·4911 (lit.,[2] n_D^{20} 1·4947).

(1RS,2RS,6RS,7SR)-2-Hydroxymethyltricyclo[5.2.1.0^{2,6}]-decane (I).—The methyl ester (III) (1·03 g, 5·2 mmol) was reduced with lithium aluminium hydride (0·19 g, 5·2 mmol) in refluxing ether. The carbinol (I) (0·77 g, 88%), purified by preparative g.l.c. (Found: C, 79·5; H, 10·9. C$_{11}$H$_{18}$O requires C, 79·45; H, 10·9%), had m.p. 74—75°, δ 0·8—2·2 (16H, complex m) and 3·55 (2H, s), $\nu_{max.}$ 3400, 2960, 2850, 1470, 1450, 1310, 1250, 1075, and 1020 cm^{-1}, m/e 148 (46%), 135 (100), 119 (10), 107 (14), 97 (15), 93 (19), 91 (15), 81 (21), 79 (30), 67 (59), and 41 (17).

(1RS,2SR,6SR,7SR)-2-Hydroxymethyltricyclo[5.2.1.0^{2,6}]-decane (VIII).—The methyl ester of (IX) was similarly reduced to give the carbinol (VIII) (83%), which was purified

by g.l.c. (Found: C, 79·7; H, 10·75%); m.p. 109—111°, δ 0·8—2·2 (16H, complex m) and 3·35 (2H, AB-type q, J 10 Hz), $\nu_{max.}$ 3400, 2950, 2380, 1470, 1045, and 1010 cm^{-1}, m/e 136 (14%), 135 (100), 134 (12), 93 (16), 91 (10), 81 (13), 79 (18), 77 (7), 67 (43), and 41 (11).

(1RS,2RS,6SR,7SR)-2-Methyltricyclo[5.2.1.0^{2,6}]decane (X).—The carbinol (VIII) (0·34 g, 2·1 mmol) was dissolved in pyridine (5 ml) and kept at 20—25° while toluene-p-sulphonyl chloride (0·50 g, 2·6 mmol) was added dropwise. The mixture was stirred overnight at ambient temperature, then poured onto 15% hydrochloric acid (20 ml) and cracked ice (20 g). The precipitate was filtered off, washed with ice-cold water, and dried in vacuo (P$_2$O$_5$) to give the crude tosylate of (VIII) (0·67 g; quantitative).

The tosylate was dissolved in tetrahydrofuran (2 ml) and added dropwise to a mixture of lithium aluminium hydride (0·08 g, 2·1 mmol) and tetrahydrofuran (10 ml) at such a rate that gentle refluxing was maintained. Refluxing was continued for a further 2·5 h. The excess of lithium aluminium hydride was destroyed by treatment with ethyl acetate followed by wet tetrahydrofuran, and the precipitate was filtered off. The filtrate was concentrated in vacuo, and the residue was purified by g.l.c. to give the methyltricyclodecane (0·15 g, 47%) (Found: C, 87·7; H, 11·85. C$_{11}$H$_{18}$ requires C, 87·9; H, 12·1%), m.p. 91—92°, δ 0·8—2·2 [complex m with sharp s at 0·99 (Me)], $\nu_{max.}$ 2950, 2850, 1485, 1470, 1460, 1375, and 1300 cm^{-1}, m/e 150 (28%, M^+), 135 (25), 108 (79), 82 (100), and 67 (96).

(1RS,2SR,6RS,7SR)-2-Methyltricyclo[5.2.1.0^{2,6}]decane (XI). —The carbinol (I) similarly gave the methyl compound (XI) as a liquid (Found: C, 87·65; H, 12·05%), δ 0·8—2·2 [complex m with sharp s at 0·94 (Me)], $\nu_{max.}$ 2950, 2850, 1475, 1460, 1375, and 1333 cm^{-1}, m/e 150 (34%, M^+), 135 (27), 109 (97), 82 (100), and 67 (90).

Hydride Transfer Reductions.—(a) The carbinol (I). The carbinol (I) (1·0 g, 6 mmol) was added to a mixture of 95% sulphuric acid (7·5 g) and n-pentane (50 ml). The mixture was stirred at 20—25° for 10 min, then set aside to allow separation of pentane layer. The sulphuric acid layer was removed and extracted with pentane (2 × 10 ml). The combined pentane layers were washed with water (3 × 20 ml), dried (CaCl$_2$), and evaporated to leave a mixture (0·23 g, 25%). G.l.c.–mass spectrometry indicated the presence of compounds (II) (91·3%), (V) (2·8%), (X) (0·6%), and (XII) (2·8%), the balance consisting of several unknown compounds. Extension of the reaction time in the hydride transfer reduction to 3 h and to 24 h resulted, without any appreciable change in the yields of the products, in the following product distributions (% at 3 and at 24 h are given in parentheses): (II) (88·5, 74·9), (V) (3·0, 4·6), (X) (0·8, 4·6), (XII) (4·4, 8·3), and 2-methyladamantane (0·5, 4·8). Compounds (V), (X), and (XII), and 2-methyladamantane were identified by comparison of g.l.c. retention times and mass spectra with those of authentic specimens. (1R,2R,5S,6S)-Tricyclo[4.3.1.1^{2,5}]undecane (II), separated and purified by preparative g.l.c., had m.p. 57·5—59° (Found: C, 87·8; H, 12·3. C$_{11}$H$_{18}$ requires C, 87·9; H, 12·1%), δ 0·8—2·4 (complex m), $\nu_{max.}$ 3025,[12] 2900, 2870, 1477, 1100, 982, 860, 795, and 750 cm^{-1}, m/e 150 (66%, M^+), 135 (51), 122 (95), 121 (34), 82 (35), 81 (51), 80 (73), 79 (58), 67 (100), and 41 (41), ^{13}C n.m.r. δ 18·4 (1C, t), 26·5 (1C, t), 28·0

[11] Z. Majerski, P. von R. Schleyer, and A. P. Wolf, J. Amer. Chem. Soc., 1970, 92, 5731.

[12] D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, J. Amer. Chem. Soc., 1961, 83, 2938; L. deVries and P. R. Rayson, J. Org. Chem., 1961, 26, 621; J. K. Stille, P. R. Kasper, and D. R. Witherell, ibid., 1963, 28, 682.

(2C, t), 28·4 (2C, t), 31·8 (1C, t), 33·2 (2C, d), and 41·2 (2C, d).

(b) *The carbinol* (VIII). The carbinol (VIII) (1·0 g, 6 mmol) similarly gave products (30% yield), of which the methyltricyclodecane (X) comprised 93%. All the rest of the products were unidentified, including some olefins and ring-fission products as judged by mass spectrometry.

Sulphuric Acid-catalysed Isomerisation of the Tricyclo-undecane (II).—The tricycloundecane (II) (0·1 g, 0·67 mmol) was mixed with 95% sulphuric acid (5 g) and carbon tetra-chloride (5 g), and the mixture was stirred at 30°. Samples were removed from the carbon tetrachloride layer and examined by g.l.c.–mass spectrometry. Almost no product was detected after 1 h. After 24 h, 17·4% of (II) had dis-appeared, to give compounds (V) (1·2%), (X) (5·8%), (XI) (0·4%), and (XII) (3·9%), 2-methyladamantane (2·8%), and unknown substances. At the end of 4 days, the product consisted of (II) (52·8%), (V) (3·4%), (X) (17·8%), (XI) (2·7%), (XII) (6·3%), and 2-methyladamantane (6·7%). 1-Methyladamantane which is reported to be formed from 2-methyladamantane under these conditions,[10] could not be identified owing to poor g.l.c. separation from unknown substances.

Isomerisation of the Methyltricyclodecane (X).—Anhydrous aluminium chloride (0·03 g, 0·2 mmol) was added to a solu-tion of compound (X) (0·15 g, 1 mmol) in methylene chloride (5 ml) at ambient temperature, and the mixture was stirred for 1 h. A sample was removed, washed with cold water, and analysed by g.l.c.–mass spectrometry. All the compound (X) had disappeared, and only three products were detected: the methyltricyclodecane (XI) (99%) and 1- and 2-methyladamantane (each 0·5%). Addition of more aluminium chloride (0·14 g, 1 mmol) and further reac-tion overnight at the same temperature transformed the reaction mixture completely into 1- and 2-methyladaman-tane (97 and 3%, respectively; almost quantitative yield).

Isomerisation of compound (X) (0·05 g, 0·3 mmol) with sulphuric acid (5 g) and carbon tetrachloride (5 g) at ambient temperature for 24 h transformed 11·3% of (X) into (XI) (0·8%) and unidentified olefinic and ring-fission products.