Syntheses of (D_3)-Trishomocubane (Pentacyclo[6,3,0,0^{2,6},0^{3,10},0^{5,9}]undecane) by Rearrangement

By Stephen A. Godleski and Paul v. R. Schleyer*
(*Department of Chemistry, Princeton University, Princeton, New Jersey* 08540)

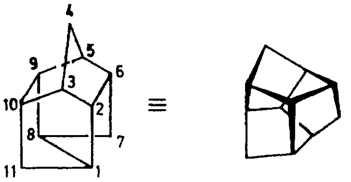
Eiji Ōsawa
(*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo* 062, *Japan*)

and Gerald J. Kent
(*Department of Chemistry, Rider College, Trenton, New Jersey* 08602)

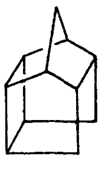
Summary (D_3)-Trishomocubane (I) can be synthesized easily by aluminum bromide-catalysed isomerization of pentacyclo[5,4,0,0,^{2,6}0^{3,10},0^{5,9}]undecane (II) or by skeletal rearrangement during aqueous HI iodination of the diol (III), followed by dehalogenation.

The chiral trishomocubane (I)[1] one of the rare organic molecules of point group D_3,[2] is the only $C_{11}H_{14}$ pentacycle not possessing three- or four-membered rings. Empirical force-field calculations[3] (those pertinent to the present work are summarized in the Table) confirm the expected greater stability of (I) over any of its pentacyclic isomers. We have synthesized (I) by taking advantage of this thermodynamic stability and have achieved a substantial improvement over the previously published route to (I).[1,4]

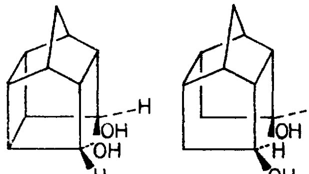
Modified Wolff–Kishner reduction of the easily accessible pentacyclic diketone (V)[5] using sodium and diethylene glycol[6] gave in 75% yield a mixture of (II)[7] (60%), (VI)† (32%), (VII)† (4·3%), and two additional olefinic products of *m/e* 146 (1·8 and 1·4%). [(VII) was identical with the Wolff–Kishner reduction product of the known diketone (VIII)[8] Hydrogenation of (VI) afforded (VII)]. Separation of the saturated (II, VII) and unsaturated fractions (VI and the two olefins with *m/e* 146) was achieved easily by chromatography on a 5% $AgNO_3$ silica gel column (80% recovery). $AlBr_3$-catalysed isomerization ($AlBr_3$ 2—3 times



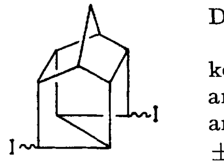
(I)



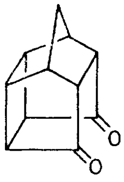
(II)



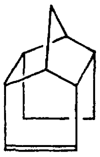
(III)



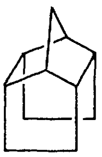
(IV)



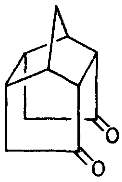
(V)



(VI)



(VII)



(VIII)

the weight of the hydrocarbon; CS_2 solvent) of the saturated fraction gave in 2 h at room temperature in 86% yield a mixture consisting of three components: (D_3)-trishomocubane (I) (93%) and two compounds of mass 148 (5 and 2%) believed to be isomeric ethanonoradamantanes. The composition of the product mixture remained invariant under more vigorous conditions (*ca.* 100 °C, longer reaction times, and a much larger excess of catalyst). Preparative gas chromatography afforded a pure sample of (D_3)-trishomocubane (I), m.p. 150—152° (lit., 147—149° [1] and 149—151° [4]). The i.r. and mass spectra of (I) are identical with those reported by Underwood and Ramamoorthy.[1] At 60 MHz, there are only two ^{1}H signals, at δ 1·96 (8H) and at 1·34 (6H).[1] The ^{13}C-n.m.r. spectrum (^{1}H decoupled) consists of three peaks, at 47·8 (6C), 41·6 (2C), and 33·3 p.p.m. (3C), as expected from the symmetry of (I), unique among saturated $C_{11}H_{14}$ isomers.

TABLE. Force-field calculations (kcal/mol, 25°)[a]

Compound	ΔH_f		Strain energy	
	Engler	Allinger	Engler	Allinger
(I)	3·38	11·32	42·05	44·13
(II)	19·62	21·93	52·29	54·74

[a] See ref. 3 for the method and for additional examples.

The second route to (I) also began with the pentacyclic diketone (V).[5] Reduction of (V) with $NaBH_4$ gave the diols (IIIa and IIIb)[5b,d] quantitatively.‡ Treatment of this diol mixture (III) with HI produced a mixture of the rearranged trishomocubyl di-iodides (IV) (93%) [m.p. 82—84°: δ 1·5 (2H, s), 2·3br and 3·1br (8H, m), and 3·9 (2H, s)]. Dehalogenation of (IV) with Zn–AcOH gave (I) in 93% yield.

Both force fields (Table)[3] predict (I) to be 10·4 ± 0·2 kcal/mol (Δ*H*) more stable than (II). Structural details are also in good agreement. The three C–C bonds lengths are calculated to be significantly different: C(1)–C(2) 1·541 ± 0·002, C(1)–C(8) 1·528 ± 0·002, and C(1)–C(11) 1·521 ± 0·003 Å (average of the results from the two different force fields[3]). All C–C–C bond angles are significantly smaller than tetrahedral; those at the three equivalent diastereotopic methylene groups are particularly strained [*e.g.*, ∠ C(1) C(11) C(10) 92·5 ± 0·5°]. All angles [(*e.g.* ∠ C(1) C(2) C(3)] at bridgeheads C(2) and C(9), which lie on the three-fold axis, are 103·4 ± 0·4°, while the angles at the six other equivalent bridgeheads are, *e.g.*: ∠ C(1) C(8) C(7) 102·7 ± 0·3°, ∠ C(1) C(8) C(9) 99·1 ± 0·1°, and ∠ C(7) C(8) C(9) 106·8 ± 0·4°. Δ Strain calculations[9] indicate that both bridgehead positions should be highly unreactive towards carbocation or free radical formation [C(2) much more so than C(1)], and this conclusion applies to methylene groups [C(4)] as well. Experimentally, we have found that (I) does not undergo a variety of substitution reactions which work well with adamantane.[10]

We thank Professors P. E. Eaton and G. R. Underwood for exchanges of information and Professor M. Saunders for the ^{13}C-n.m.r. spectrum of (I). This work was supported by grants from the National Institutes of Health and from Hoffmann-La Roche, Nutley, New Jersey.

(*Received*, 13*th August* 1974; *Com.* 1046.)

---

† All new compounds gave satisfactory elemental analyses.

‡ A large excess of $NaBH_4$ was used to reduce the ketol,[5b] portions being added over a 2 day period with warming.

[1] G. R. Underwood and B. Ramamoorthy, *Tetrahedron Letters*, 1970, 4125. The ^{1}H-n.m.r. chemical shifts are reported incorrectly in this paper (G. R. Underwood, personal communication).

[2] M. Farina and C. Morandi, *Tetrahedron*, 1974, **30**, 1819.

[3] E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8005.

[4] P. E. Eaton, R. A. Hudson, and C. Giordano, following communication, have developed an alternative synthesis particularly suited to (D_3)-trishomocubanone.

[5] (a) R. C. Cookson, E. Crundwell, and J. Hudec, *Chem. and Ind.*, 1958, 1003; (b) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 1964, 3062; (c) J. R. Scheffer, J. Trotter, R. A. Wostradowski, C. S. Gibbons, and K. S. Bhandari, *J. Amer. Chem. Soc.*, 1971, **93**, 3813; (d) G. R. Underwood and B. Ramamoorthy, *Chem. Comm.*, 1970, 12.

[6] D. H. R. Barton, D. A. J. Ives, and B. R. Thomas, *J. Chem. Soc.*, 1955, 2056. In our hands, Wolff–Kishner reduction of (V) by a procedure similar to that reported recently [7a] gave unsatisfactorily low yields.

[7] (a) A. P. Marchand and R. W. Allen, *J. Org. Chem.*, 1974, **39**, 1596; (b) J. R. Stedman, L. S. Miller, L. D. Davis, and J. R. E. Hoover, *ibid.*, 1970, **35**, 4169.

[8] E. Wenkert and J. E. Yoder, *J. Org. Chem.*, 1970, **35**, 2986.

[9] R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 3189.

[10] See E. M. Engler and P. v. R. Schleyer, 'M.T.P. Review of Science, Organic Chemistry,' Series I, Butterworths, London, 1973, Vol. 5, ch. 7, p. 239 and earlier reviews.