Synthesis of [8]Tritwistane† (Pentacyclo[8.4.0.$0^{2,7}$.$0^{3,12}$.$0^{6,11}$]tetradecane

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Summary The first synthesis of [8]tritwistane, which has D_3 symmetry, is reported.

ALTHOUGH numerous methods for preparing adamantane derivatives have been studied, syntheses of the twistane series of compounds have hardly been developed. Previously a convenient method for the synthesis of ditwistane, a homologue of twistane, was established in our laboratory using catalytic hydrogenation as the key step.[1] [8]Tritwistane, the next highest homologue of ditwistane, is one of the few compounds belonging to the chiral point group D_3,[2] and its synthesis is quite important for chiroptic studies.[3] We have now synthesised [8]tritwistane from cyclohexa-1,3-diene in 34% overall yield.

The diketone (**1**), easily accessible from cyclohexa-1,3-diene–*p*-benzoquinone Diels–Alder adduct by photocyclization,[4] was reduced with $NaBH_4$ to give the acetal (**2**)‡ (100%, m.p. 193—194 °C). Treatment of (**2**) with 47% HBr (110 °C, 13 h) produced the rearranged bromoketone (**3**) (87%, m.p. 83—86 °C) and the dibromoalcohol (**4**)

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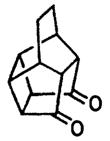
† Trivial name proposed by Schleyer *et al.*; *cf.* W. D. Graham, P. von R. Schleyer, E. W. Hagamane, and E. Wenkert, *J. Am. Chem. Soc.*, 1973, **95**, 5785.

‡ All new compounds gave satisfactory spectral and elemental analyses.



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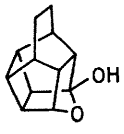

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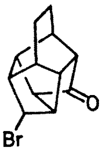

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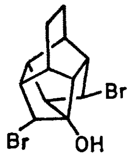

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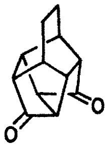

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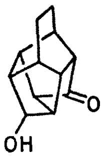

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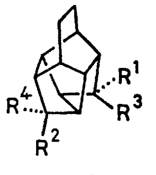
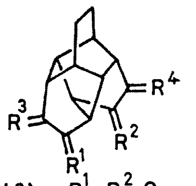
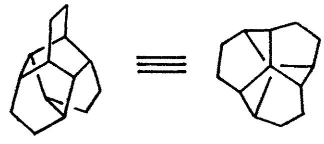




(7) a; $R^1 = R^2 = OH$
$R^3 = R^4 = CHBr_2$
b; $R^3 = R^4 = OH$
$R^1 = R^2 = CHBr_2$
c; $R^1 = R^4 = OH$
$R^2 = R^3 = CHBr_2$

(8) a; $R^1 = R^2 = O$
$R^3 = R^4 = H_2$
b; $R^3 = R^4 = O$
$R^1 = R^2 = H_2$
c; $R^1 = R^4 = O$
$R^2 = R^3 = H_2$



(9)

(10%, m.p. 121—122 °C). Oxidation of (**3**) with dimethyl sulphoxide in the presence of $AgClO_4$ gave the diketone (**5**) (66%, m.p. 195—197 °C) and the hydroxy ketone (**6**) (22%, m.p. 180—181 °C). Since (**6**) can be readily converted almost quantitatively into (**5**) by chromic acid oxidation, the conversion of (**3**) into (**5**) is quite efficient. The structural assignment of a symmetrical framework to (**5**) follows from its ^{13}C n.m.r. spectrum ($CDCl_3$): δ 17·55 (t), 31·59 (d), 32·73 (d), 41·00 (d), 45·44 (d), and 209·12 (s) p.p.m.

Expansion of the two cyclopentanone rings in (**5**) was stereospecifically achieved by the application of Nozaki's procedure.[5] Thus, (**5**) reacted with CH_2Br_2 and lithium dicyclohexylamide in tetrahydrofuran (THF)–ether at −100 °C to give the tetrabromide (**7**) [83%, m.p. 279—281 °C (decomp.)], as sole product. This tetrabromide, on treatment with Bu^nLi in THF at −78 °C gave the desired diketone (**8**) [82%, m.p. 152—154 °C]. Compounds (**7**) and (**8**) must have the structures (**7a**) or (**7b**) and (**8a**) or (**8b**), respectively for the following reasons. The unsymmetrical (**7c**) and (**8c**) can be excluded easily by their ^{1}H n.m.r. spectra {(**7**) [$(CD_3)_2SO$]: δ 1·41 (br s, 4H), 1·84 (d, *J* 6 Hz, 2H), 2·04 (d, 6 Hz, 2H), 2·34 (m, 2H), 2·62 (m, 2H), 5·64 (s, 2H), and 6·28 (s, 2H); (**8**) ($CDCl_3$): δ 1·65 (m, 2H), 1·70 (s, 4H), and 2·1—2·7 (m, 10H)}. Compound (**8**) was converted into tritwistane (**9**) (76%, m.p. 100—102 °C) by desulphurization of the thioacetal of (**8**) (87%, m.p. 168—169 °C). The mass spectrum of (**9**) is characterized by a molecular ion peak at *m/e* 188 (100%) in addition to moderately intense peaks at *m/e* 173(14%), 161(23), 148(21), 131(21), 93(30). and 80(26). The ^{1}H and ^{13}C n.m.r. spectra of (**9**) in $CDCl_3$ attest D_3 symmetry of the molecule. At 270 MHz, there are three ^{1}H signals at δ 1·49 (m, 6H), 1·56 (m, 12H), and 1·75 (m, 2H). The ^{13}C-n.m.r. spectrum consists of only three peaks at δ 23·42 (t), 31·09 (d), and 35·96 (d) p.p.m.

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