Trishomocubanone (Pentacyclo[6,3,0,$0^{2,6}$,$0^{3,10}$,$0^{5,9}$]undecan-4-one)

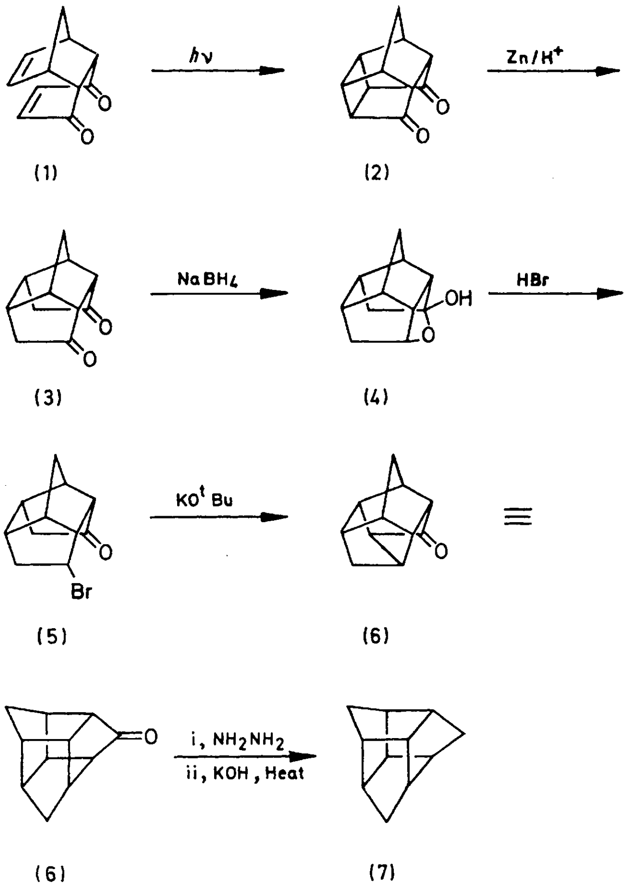
By PHILIP E. EATON,* RICHARD A. HUDSON, and CLAUDIO GIORDANO
(*Searle Chemistry Laboratory, The University of Chicago, Chicago, Illinois* 60637)

Summary A method is outlined for the conversion of the cyclopentadiene–quinone Diels-Alder adduct into trishomocubanone and trishomocubane.

WE have found a direct synthetic route to trishomocubanone (**6**). [1] The pentacyclic framework of this ketone, unlike that in most other highly condensed cage systems, contains no cyclobutane rings: the skeleton is constructed of five-membered rings. It is intrinsically chiral. Trishomocubanone is a key member of the system as the carbonyl group provides a ready 'handle' for optical resolution and for the introduction of other functional groups.

Unlike other entries into the trishomocubane system our synthesis does not involve a carbonium ion rearrangement.[1b,c] The well known cage compound (**2**), produced by photocyclization of the cyclopentadiene-*p*-benzoquinone Diels-Alder adduct (**1**),[2] is reduced with Zn-AcOH to the tetracycle (**3**).[1a,3] Reduction of (**3**) with $NaBH_4$ in aqueous EtOH gives, in nearly quantitative yield, the hydroxyketone as the internal hemiacetal (**4**), m.p. 223–223·5° (from hexane). Treatment of (**4**) with excess of 32% HBr in AcOH at 100° for 8 h under pressure gives at least 64% of the bromoketone (**5**), m.p. 63—65° (from hexane), ν_{max} (CCl_4) 1748 cm^{-1}. This bromoketone reacts quantitatively at room temperature with a suspension of $KOBu^t$ in anhydrous Et_2O to produce the title ketone (**6**), m.p. 163—164° after sublimation, ν_{max} (CCl_4) 1785 (sh), 1778, and 1757 cm^{-1}, 2,4-dinitrophenylhydrazone m.p. 207·5—208·5 (from MeCN). Wolff-Kishner reduction of (**6**) using standard Huang-Minlon conditions gives the hydrocarbon (**7**), m.p. 149—151° (from MeCN) (lit.,[1b] 147—149°).

The ^1H and ^{13}C n.m.r. spectra of (**6**) and (**7**) are completely consistent with the structural assignments. Compound (**6**), ^1H n.m.r. (270 MHz; $CDCl_3$) δ 2·47 (2H, $W_{\frac{1}{2}}$ *ca.* 12 Hz), 2·40 (4H, $W_{\frac{1}{2}}$ *ca.* 7 Hz), 1·79 (2H, $W_{\frac{1}{2}}$ *ca.* 10 Hz), 1·69 (2H, d, *J* 10·5 Hz), and 1·43 (2H, d, *J* 10·5 Hz); ^{13}C n.m.r. (22·63 MHz; proton-decoupled; $CDCl_3$) δ (from Me_4Si) 217·3(w), 50·2, 47·6, 41·1, 40·9, and 35·5 p.p.m. (intensity of upper 5 lines approximately equal). Compound (**7**), ^1H n.m.r. (270 MHz; $CDCl_3$) δ 2·0 (6H, $W_{\frac{1}{2}}$ *ca.* 10 Hz), 1·8 (2H, $W_{\frac{1}{2}}$ *ca.* 15 Hz), and 1·32 (6H, $W_{\frac{1}{2}}$ *ca.* 3 Hz); ^{13}C n.m.r. (22·63 MHz; proton-decoupled; $CDCl_3$) δ 47·7, 41·5, and 33·2 p.p.m., intensity ratio roughly 6:2:3. The presence of only three resonances in the proton-decoupled ^{13}C n.m.r. spectrum of (**7**) establishes unambiguously the arrangement of the methano-bridges in this trishomocubane as shown. Other permutations would give rise to five or more resonances in the ^{13}C spectrum. (There are altogether nine possible arrangements of the methano bridges, excluding mirror images).



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[1] (a) Entry into this ring system was reported first by one of us at the 155th Meeting of the American Chemical Society, San Francisco, April, 1968. The method presented then was a primitive version of that described here. (b) Another approach to the ring system (but not the ketone) has been given by G. R. Underwood and B. Ramamoorthy (*Tetrahedron Letters*, 1970, 4125). (c) P. v. R. Schleyer, S. A. Godleski, E. Osawa, and G. J. Kent, preceding communication, have synthesised trishomocubane by $AlBr_3$-isomerization of the hydrocarbon derived from (**2**). We thank Dr. Schleyer for informing us of this result prior to publication.

[2] R. C. Cookson, E. Crundwell, and J. Hudec, *Chem. and Ind.*, 1958, 1003.

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