**Significance:** Cubane (9) is a highly strained hydrocarbon in which eight carbon atoms are arranged at the corners of a cube, adopting unusually 90° bonding angles. Before it was first synthesized in 1964 by Eaton and Cole, researchers believed that such cubic carbon-based molecule would be too unstable to exist. Initially, cubane was considered just a laboratory curiosity of interest only to academics, however, over time this remarkable hydrocarbon and derivatives have found applications in controlled energy storage, the explosives industry, pharmaceuticals, and polymer science.

**Comment:** The classic synthesis of cubane starts from 2-cyclopentenone and consists of fifteen discrete steps with an overall yield of about 5%. There are three key synthetic elements: (a) the highly endo-selective Diels–Alder reaction of 2-bromocyclopentadienone (1) generated in situ, producing the endo-dimer 2 (J. Am. Chem. Soc. 1964, 86, 962); (b) the [2+2] photocyclization of 3, obtaining 4; and (c) the double Favorskii ring contraction of the cage diones 4 and 7, producing 5 and 8, respectively. Nowadays, the chemistry of cubane is well developed and it can be easily obtained on a multi-gram scale (see Review below).