**Significance:** Dexamethasone is a corticosteroid that was first synthesized in 1957 and was approved in 1961 for the treatment of a wide range of inflammatory disorders. It is on the WHO List of Essential Medicines. In June 2020, dexamethasone was given preliminary approval for the treatment of COVID-19 because it improved survival rates of hospitalized patients receiving oxygen or on a ventilator. In 1997, Furukawa and co-workers reported a synthesis of dexamethasone from tigogenin.

**Comment:** For the introduction of the 17α-hydroxy-16α-methyl moiety (B $\rightarrow$ E) the key epoxidation reaction was accomplished with peracetic acid in a buffer solution of sodium acetate and acetic acid (95% overall yield). Then the introduction of the 1,4-diene in the A-ring (H $\rightarrow$ J, 83% yield) was greatly improved by bromination–dehydrobromination, in which dehydrobromination proceeded smoothly in a mixture of DMF and 6% of water (83% yield).