Resistance of Adamantanone to Homoenolization

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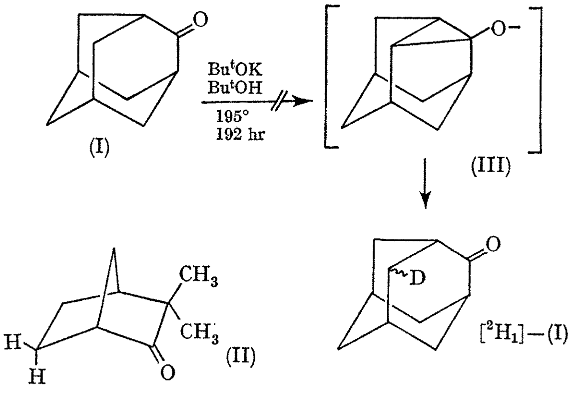
Summary Adamantanone (I) undergoes no homoenolization under conditions favourable to this process in camphenilone (II).

NICKON and his co-workers[1] have demonstrated that a ketone function may in suitable cases activate proton abstraction from a β-position, resulting in the formation of a homoenolate anion which exhibits cyclopropoxide symmetry in reverting to ketone under protonolysis.[2] Adamantanone (I) constitutes a suitable system for further investigation of the structural limitations of homoenolization. Its α-hydrogen atoms should be non-enolizable by virtue of their orthogonal orientation to the carbonyl π-bond, and its eight β-protons bear two fixed geometric relationships to the ketone group. We report here that adamantanone (I) does not undergo appreciable homoenolization under conditions which lead to preponderant homoenolization in camphenilone (II).



A solution of adamantanone[3] (I) and potassium t-butoxide both 0·50 molar in $[O\text{-}^2H_1]$-t-butyl alcohol (90% deuteriated) was maintained at 195 ± 2° for 192 hr. The ^1H n.m.r. spectrum[4] of the recovered (87·5%) ketone showed no apparent deuterium incorporation in either the α- or β-positions. The result was precisely confirmed by 70 ev mass spectrometry. Adamantanone (I) was found to give rise to a prominent molecular ion base peak (*m/e* 150), with $100(P + 1)/P = 11{\cdot}08 \pm 0{\cdot}16$ as expected for natural isotopic abundances.[5] For the treated ketone, the intensity ratio for the same *m/e* signals was $11{\cdot}13 \pm 0{\cdot}14$.

By comparison, the half-life for deuterium exchange into camphenilone (II) under similar concentration conditions at 185° is approximately 20 hr.[2] The low reactivity of adamantanone reflects the severe strain that would be incurred in formation of intermediate (III). The results correlate qualitatively with internuclear distances in the parent hydrocarbons, as given in (IV)[6] and (V),[7] and with the compact tricyclic nature of adamantanone (I). The heat of hydrogenation of nortricyclane (VI) to norbornane (IV) has been deduced[8] to be −32·1 kcal./mole, but data have not yet been reported for the corresponding conversion of dehydroadamantane[9] (VII) into adamantane (V).

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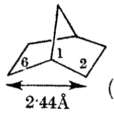

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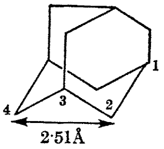

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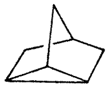
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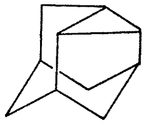
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