

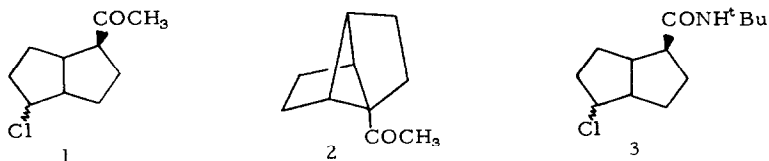
REACTION OF 2-ACETYL-6-CHLORO-CIS-BICYCLO[3.3.0]OCTANE WITH BASE

John N. Labows, Jr.

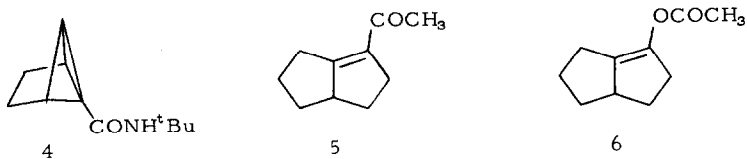
Department of Chemistry, Wilkes College
Wilkes-Barre, Pennsylvania 18703

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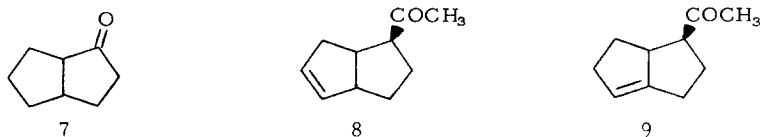
A properly substituted bicyclo[3.3.0]octane, such as *exo*-2-acetyl-6-chloro-*cis*-bicyclo[3.3.0]octane (1),⁽¹⁾ could lead on base treatment via a ring closure of the 2, 6 positions to a tricyclo[3.3.0,0^{2,6}]octane derivative (2). This approach was first attempted when *t*-butyl-carboxamide-6-chloro-*cis*-bicyclo[3.3.0]octane (3), prepared from 1 via the acid, was reacted with butyl lithium in a reaction analogous to that used for the preparation of



tricyclo[3.1.0,0^{2,6}]hexane-5-*t*-butyl carboxamide (4).⁽²⁾ However, in this case the reaction of 3 gave a major product in which the chlorine was replaced by a hydrogen.⁽³⁾

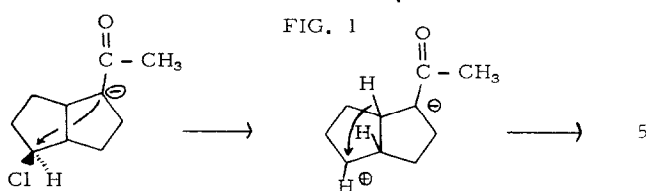


In a bromoform reaction of 1, a neutral product was isolated which had lost the elements of hydrogen and chlorine. Subsequent reactions of 1 with either aqueous sodium hydroxide at room temperature or sodium methoxide in methanol at reflux led to the formation of one major product identified as 2-acetyl-bicyclo[3.3.0]oct-1-ene (5). The nmr spectrum of 5 showed peaks only from 7.0 to 9.0 τ , while the infrared spectrum showed strong absorption at 5.99 μ .⁽⁴⁾ Compound 5 failed to undergo hydrogenation at room temperature and atmospheric pressure. On Baeyer-Villiger oxidation with *m*-chloroperbenzoic acid, 5 was converted into an ester (6) which on treatment with base gave the known bicyclo[3.3.0]octan-2-one (7).⁽⁵⁾



Two minor products, formed on prolonged treatment of 1 with sodium methoxide (eight days), were identified as 2-acetyl-bicyclo[3.3.0]oct-6-ene (8) (nmr 4.5 τ (2), 6.8-8.6 τ (9), 8.0 τ (3), and ir 5.86 μ) and 2-acetyl-bicyclo[3.3.0]oct-5-ene (9) (nmr 4.5 τ (1), 6.8-8.4 τ (10), 8.0 τ (3), and ir 5.84 μ). Hydrogenation at atmospheric pressure over Adams catalyst of a mixture of 5, 8, and 9 gave unchanged 5 and a new product characterized as the known *exo*-2-acetyl-*cis*-bicyclo[3.3.0]octane.⁽⁶⁾

The original compound 1 gives two overlapped peaks on glpc indicating the presence of both the *exo* and *endo* chloro isomers. If it is assumed that the *exo* isomer is present in larger amounts and also has the longer retention time,⁽⁷⁾ then the immediate decrease in the intensity of that peak on base treatment suggests that the *exo* isomer is more reactive than the *endo* isomer; an interesting result when compared to the stability of other 6-*exo*-chloro bicyclo[3.3.0]octane derivatives to strongly basic conditions.⁽⁸⁾ An explanation of this behavior would implicate a carbanion in 1 at carbon 2 assisting in some way in the elimination of the chloride ion. An internal S_N2 type displacement of halide ion, though discounted in the Favorskii reaction because of the necessity of breaking the orbital overlap of the enolate ion,⁽⁹⁾ may exist here because it is not necessary for rotation to occur for the p orbital at carbon 2 to interact with carbon 6. A positive charge at carbon 6 could then be followed by a 1,3-hydrogen shift leading to 5, (Fig. 1).



The formation of products 8 and 9 can be explained by means of a *trans* elimination of (a) the *endo* chloro isomer by abstraction of the proton at carbon 5 and (b) the chlorine by abstraction of the proton at carbon 7. Attempts to isomerize compounds 8 and 9 to 5 with sodium hydroxide were unsuccessful.

Thus, it appears that interaction of carbon positions 2 and 6 has occurred but that no bond formation is observed possibly due to the necessary introduction of strain in 2 or

its instability under the reaction conditions. An attempt to study the reaction under less vigorous conditions as well as the kinetics of the reaction is in progress.

References:

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