

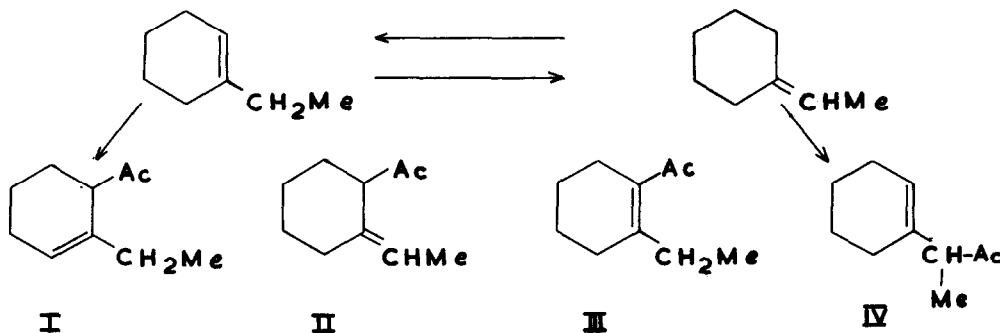
THE ACETYLATION OF 1-ETHYLCYCLOHEXENE

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The zinc chloride catalysed acetylation of 1-ethylcyclohexene has been reported¹ to afford 6-acetyl-1-ethylcyclohexene (I) together with 1-acetyl-2-ethylidene-cyclohexane (II) as a minor product. More recently Allard and Dufort have reported² that the stannic chloride catalysed acetylation of 1-ethylcyclohexene affords I (43%), II (36%), and 1-acetyl-2-ethylcyclohexene (III, 12%).



In the above studies the exocyclic unsaturated ketone (II) was reported to exhibit an NMR doublet at ca. τ 8.9. This unusually high field value for a vinylic methyl group prompted us to re-examine this compound, and we now report that (IV) represents the correct structure. Treatment of the compound with deuterium oxide/dioxan/sodium methoxide afforded a ketone which was gas-chromatographically indistinguishable from the starting material. The IR spectrum exhibited several differences, notably the removal of the CH_2CO deformation band at 1360 cm^{-1} . The NMR spectrum showed that all protons δ to the carbonyl group had been replaced by deuterium. The olefinic proton had undergone little or no exchange but the

methyl group absorption had collapsed to a singlet (slight H-D coupling was apparent). These observations preclude structure (II) and are entirely consistent with the structure 2,1'-cyclohexenyl-3-oxo-butane (IV).

The acetylation of 1-ethylcyclopentene has also been incorrectly reported³ to afford 1-acetyl-2-ethylidene-cyclopentane as a minor product. The spectral properties of the product are in accord with the structure 2-1'-cyclopentenyl-3-oxo-butane.

Exocyclic $\beta\gamma$ -unsaturation does occur in certain acylation products⁴, thus 1-methylcycloheptene affords 7-acetyl-1-methylcycloheptene (44%) and 1-acetyl-2-methylene-cycloheptane (25%). The latter compound has $\nu_{C=O}$ 1706 cm^{-1} and NMR bands at τ 4.98 and 5.06 (two doublets, C = CH_2 , J = 1Hz); 6.85 (m, CH - COCH_3) and 7.88 (s, COCH_3). The acetylation of 1-methylcyclooctene affords 1-acetyl-2-methylene-cyclooctane (45%), 8-acetyl-1-methylcyclooctene (12%) and an unidentified non-conjugated ketone (11%) which probably arises from a transannular hydride shift⁵. The exocyclic unsaturated ketone has $\nu_{C=O}$ 1705 cm^{-1} , and NMR bands at τ 4.87 and 5.00 (two doublets, C = CH_2 , J = 1Hz); 6.80 (m, CH - COCH_3) and 7.94 (s, COCH_3). Further proof of structure was obtained by reaction with ozone followed by hydrogenation over palladium/calcium carbonate to afford formaldehyde.

Satisfactory analyses were obtained for all the compounds reported in this paper.

References

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