

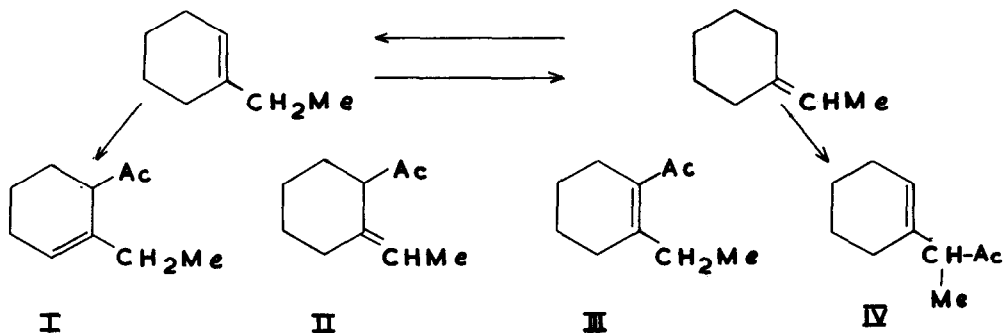
THE ACETYLATION OF 1-ETHYLCYCLOHEXENE

J. K. Groves and N. Jones

Department of Chemistry and Metallurgy, Lanchester Polytechnic, Coventry, CV1 5FB.

(Received in UK 5 February 1970; accepted for publication 19 February 1970)

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 The NMR spectrum showed that all protons α to the carbonyl group had been replaced by deuterium.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 $\beta\delta$ -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 $\nu_{\text{C=O}}$ 1706 cm^{-1} and NMR bands at τ 4.98 and 5.06 (two doublets, C = CH₂, J = 1Hz); 6.85 (m, CH - COCH₃) and 7.88 (s, COCH₃). 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 $\nu_{\text{C=O}}$ 1705 cm^{-1} , and NMR bands at τ 4.87 and 5.00 (two doublets, C = CH₂, J = 1Hz); 6.80 (m, CH - COCH₃) and 7.94 (s, COCH₃). 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

1. J. K. Groves and N. Jones, J. Chem. Soc. (C), 2215 (1968).
2. J. Allard and N. Dufort, Canad. J. Chem., 47, 2403 (1969).
3. J. K. Groves and N. Jones, J. Chem. Soc. (C), 608 (1969).
4. J. K. Groves, Ph.D. Thesis, Lanchester College of Technology (1969).
5. J. K. Groves and N. Jones, J. Chem. Soc. (C), 1708 (1969).