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# THE ACID CATALYSED EQUILIBRATION OF 4-ALKYLCYCLOHEX-3-ENONES AND 4-ALKYL-CYCLOHEX-2-ENONES.

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The acid or base catalysed conversion of a non-conjugated unsaturated carbonyl compound into the conjugated isomer has been frequently used in synthetic procedures. There have been various reports of reactions where the conversion was incomplete or even where no rearrangement appeared to occur (1). As part of a survey of the acid catalysed rearrangement of a series of unsaturated cyclic ketones we have examined the following equilibrium.

(I) (II)

(where R = H, $CH_3$, $CH_3.CH_2$, $(CH_3)_2.CH$, and $(CH_3)_3.C$)

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The β,γ-unsaturated ketones were prepared from the corresponding anisole by Birch reduction and subsequent decomposition of the dihydroanisole with aqueous sodium bisulphite (2). The ketones prepared in this way had a single non-conjugated carbonyl absorption band in the i.r. region, showed no conjugated u.v. absorption, and gave a single peak on gas chromatography. The ketones were equilibrated with 2N sulphuric acid under reflux and the recovered ketone mixture was analysed by gas chromatography. In two cases (R = $CH_3.CH_2$ and $(CH_3)_2CH$) the equilibrium mixture was also obtained by acid treatment of the α,β-unsaturated isomer.

Only two peaks were recorded for each equilibrated sample and in each case the 2,4-dinitrophenylhydrazone of the conjugated isomer was isolated after treatment of the reaction mixture with 2,4-dinitrophenylhydrazine. The percentage compositions of the mixtures at equilibrium are reported in the Table. The reproducibility of the analyses was about ±2%. The equilibrium value for the 4-isopropylcyclohexenone system is in reasonable agreement with the value previously recorded by Soffer and Williston (1b).

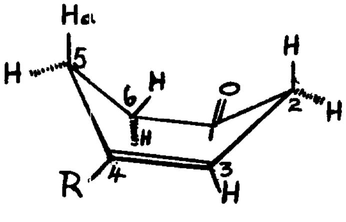
TABLE

| 4-substituent (R) | $\beta,\gamma$-unsaturated ketone (I) | $\alpha,\beta$-unsaturated ketone (II) |
|---|---|---|
| H | 0 | 100 |
| $CH_3$ | 30 | 70 |
| $CH_3.CH_2$ | 30 | 70[a] |
| $(CH_3)_2.CH$ | 40 | 60[a] |
| $(CH_3)_3.C$ | 50 | 50 |

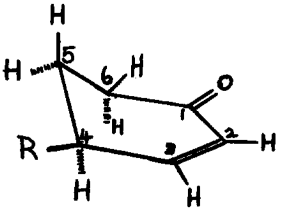
[a] Equilibrium mixture obtained by the equilibration of both (I) and (II)

It has been suggested (1b,1c) that the equilibrium between (I) and (II) is governed by (a) conjugation of the carbonyl and ethylene groups and (b) the possibility of hyperconjugation with the ethylenic system. On this basis the decreasing possibility of hyperconjugation in the ketone (I) as R changes from $CH_3$ to $(CH_3)_3C$ would be expected to decrease the stability of (I) with respect to (II) and so to decrease the percentage of (I) found at equilibrium. The observed trend of results is in just the opposite direction with the greatest percentage of (I) being found with the tertiary butyl substituent, and thus some other factor would appear to be involved. It is suggested that steric interactions are responsible for the observed results.

It has been stated (3) that in tne cyclohex-2-enone system all the ring carbons except $C_5$ are



(A)



(B)

approximately planar [e.g. (B)]. Two such conformations are possible in which the R substituent at $C_4$ is essentially axial or equatorial and presumably the conformer with R equatorial is the more stable one. In such a conformation, (B), a substituent R is subject to steric interaction with the two hydrogen atoms at $C_5$ and with the vinylic hydrogen at $C_3$. In addition there is 1:3-diaxial interaction of the hydrogens at $C_4$ and $C_6$. For the $\beta,\gamma$-unsaturated ketone, it would appear, from examination of models, that the ring takes up a non-flexible, flattened, boat form (4) as in (A). Two interconvertible conformations of this structure are possible but these are non-superposable mirror image conformations where the spatial environment of the 4-alkyl group is unaffected. The group R is subject to three interactions with hydrogen atoms on adjacent carbons, one at $C_3$ and two at $C_5$, but one of these, R to $H_{5(a)}$, would appear to be essentially negligible. In this flattened boat form the unfavourable flagpole interactions of the normal boat conformation are absent, as the two corresponding C-H bonds [attached to $C_2$ and $C_5$ in (A)] are approximately parallel. No 1,3-diaxial interactions are present.

There would thus appear to be greater steric interference in the conjugated form (II) than in the non-conjugated isomer (I) and consequently as the 4-substituent increases in size the difference in the stabilities of conjugated and non-conjugated forms should decrease. This should lead to an increase in the equilibrium percentage of non-conjugated isomer with increase in size of R as is observed experimentally.

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