References and Notes

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Equilibria between α,β- and β,γ-Unsaturated Ketones in Six-Membered Rings Fused β,γ to Five-, Six-, and Seven-Membered Rings

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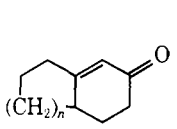
The equilibria between α,β- and β,γ-unsaturated ketones have been determined for a series of bicyclic ketones **2**, **4**, and **8** and **3**, **5**, and **9**. Alkylation on the α position increases the percentage of β,γ-unsaturated isomer at equilibrium. Steric and hyperconjugation effects in these and other acyclic and cyclic unsaturated ketones, esters, carboxylic acid salts, and nitriles are discussed.

In the course of the synthetic work described in the preceeding paper,[1] we encountered several α,β-unsaturated ketones in which the percentage of β,γ-unsaturated isomer present, even after equilibration, seemed significantly high. Accordingly, we undertook a systematic study of the available unsaturated ketones.

It has long been recognized that α,β-unsaturated carbonyl compounds, when treated with acid or base, tautomerize to a mixture of α,β- and β,γ-unsaturated isomers. The earliest work was that of Kon and Linstead, who investigated alkali catalyzed equilibria in series of acyclic unsaturated carboxylic acids[2-8] **17a/18a**, cyanides[9-10] **17b/18b**, and ethyl esters[5,11] **17c/18c**. This work has been summarized with the assistance of Linstead.[12] Unsubstituted carboxylic acid salts and esters equilibrate to give almost exclusively the α,β isomer. One γ-alkyl substituent will shift the equilibrium toward the β,γ isomer, while two γ substituents will suffice to make the β,γ isomer predominate. Substitution on the β carbon seems, from limited evidence in the acid series, to favor the β,γ isomer, but not to the same degree as a γ substituent. α-Substitution in the carboxylic acid series moderately favors the α,β isomer.



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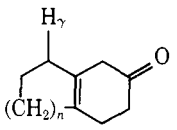
b, $n = 2$
c, $n = 3$



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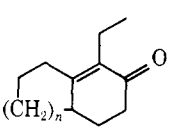

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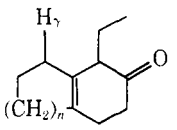

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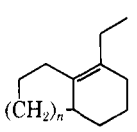

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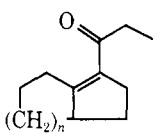

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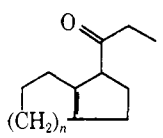
c, $n = 3$



9a, $n = 1$
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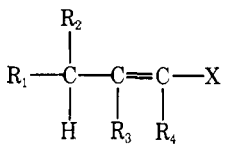
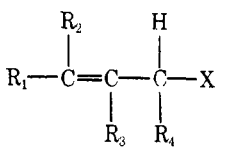
c, $n = 3$



17a, $X = CO_2^-$
b, $X = CN$
c, $X = CO_2Et$
d, $R_1 = R_3 = R_4 = H$; $R_2 = Et$; $X = COCH_3$
e, $R_1 = Et$; $R_3 = H$; $R_4 = Me$; $X = CO_2Et$



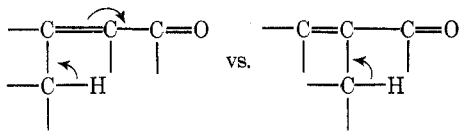
18a, $X = CO_2^-$
b, $X = CN$
c, $X = CO_2Et$
d, $R_1 = R_3 = R_4 = H$; $R_2 = Et$; $X = COCH_3$
e, $R_1 = Et$; $R_3 = H$; $R_4 = Me$; $X = CO_2Et$

In an acyclic ketone experiment, Eccott and Linstead[13] reported an equilibrium composition of 25% β,γ isomer, 75% α,β isomer for the heptenones **17d/18d**, and it has been stated[12] that β- and γ-substitution affect the equilibrium in ketones much as in the acid and ester series, but that α-substitution also shifts the equilibrium toward the α,β isomer, in contrast to the carboxylic acid series. The basis of this statement is not clear.

That a γ-alkyl substituent should stabilize the β,γ isomer is not surprising, and Rinehart and Dolby[14] have shown that for the ethyl esters **17e/18e**, the percentage of α,β isomer is 45% for R_2 = Me, 68% for R_2 = Et, 78% for R_2 = *i*-Pr, and 86% for R_2 = *t*-Bu, the order to be expected if hyperconjugation is the major factor stabilizing the β,γ double bond. There must, of course, also be some steric factors involved in the above series. Dolby and Riddle[15] have very carefully examined the equilibria for a series of unsaturated esters **19/20**, where the hyperconjugative effects are transmitted through the phenyl ring, and where steric effects are essentially the same in all members of the series. Again, the order predicted on the basis of hyperconjugation is found; the percentage of α,β-unsaturated isomer at equilibrium, using sodium ethoxide in ethanol at 77 °C, was 59% where R = H, 40% where R = Me, 46% where R = Et, 50% where R = *i*-Pr, and 52% where R = *t*-Bu. Bateman and Cuneen[16] used stabilization factors derived from equilibrations of γ-alkylphenylpropenes to quantitatively evaluate the equilibria studied by Kon and Linstead, with some success.

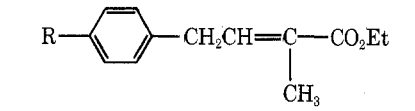
A β-alkyl substituent will stabilize the double bond in both the α,β- and β,γ-unsaturated isomers. Bateman and Cuneen used the same stabilization factor for hyperconjugation between an alkyl group and a nonconjugated double bond and between an alkyl group and either carbon of the C–C double bond of a conjugated system. Hence, their analysis predicts that a β substituent will not change the equilibrium. The fact that such a substituent does change the equilibrium in favor of the β,γ isomer (at least in cases where there is also a γ substituent) suggests that hyperconjugative stabilization of the nonconjugated double bond is greater.

Hyperconjugation due to an α-alkyl substituent on an α,β-unsaturated carbonyl (or similar) system may well not be as powerful a stabilizing force as hyperconjugation at a terminal (β) position. In the latter case, the hyperconjugation is



supplying electrons to a carbon which is clearly becoming electron deficient. Unfortunately, insufficient experimental evidence is available on this point.

In cyclic systems, steric effects can be much more important than in acyclic systems. Kon and co-workers examined the equilibria between the cycloalkylidene methyl ketones **21** (α,β unsaturated) and the cycloalkenyl methyl ketones **22** (β,γ unsaturated). The five-membered ring compounds **21a/22a** equilibrated to 77% α,β isomer,[17,18] the six-membered ring ketones **21b/22b** to 23% α,β isomer,[19] and the seven-membered ring ketones **21c/22c** to 60% α,β isomer.[18,20] These equilibria were obtained first in alkaline conditions, but later the same results were obtained under acid conditions.[21] Clearly, conformational effects are the controlling influence in these ketones. Presumably the added angle strain of a second sp^2 carbon mitigates against the β,γ isomer in the five-membered ring. In comparing the exocyclic (α,β isomer) and endocyclic (β,γ isomer) double bonds in the six-membered ring, the cyclohexane ring in the α,β isomer **21b** adopts approximately a chair conformation,[22] with 1,3-diaxial interactions between C-2 and C-4, C-2 and C-6, C-4 and C-6, and C-3 and C-5. The β,γ isomer **22b** adopts the flattened cyclohexene conformation,[23] with only two 1,3-diaxial interactions (C-4, C-6 and C-3, C-5). This difference is apparently enough to shift the equilibrium so that it favors the β,γ isomer. The seven-membered ring with the exocyclic double bond (α,β isomer **21c**) shows a conformation (see diagram) with 1,3-diaxial interactions between C-3 and C-5, C-4 and C-6, and C-5 and C-7, with the C-3, C-5 interaction being increased by the hydrogens being pointed toward each other. There is also a C-3 and C-7 1,4-diaxial interaction. The β,γ isomer **22c** (see diagram) has normal 1,3-diaxial interactions between C-3 and C-5, C-4 and C-6, and C-5 and C-7. It also has a C-3 and C-7 1,4-diaxial interaction. Thus, the β,γ isomer is favored only because of the abnormally severe C-3 and C-5 interaction in the α,β isomer. It does appear then that Kon's results can be explained using conformational factors.



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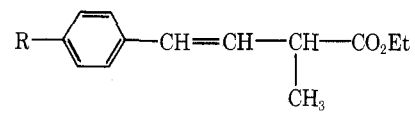

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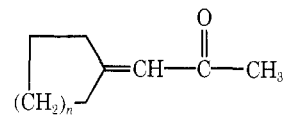
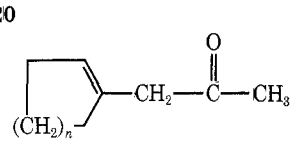


21a, $n = 1$
b, $n = 2$
c, $n = 3$



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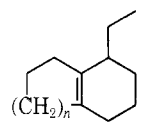
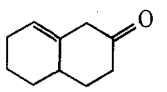
b, $n = 2$
c, $n = 3$

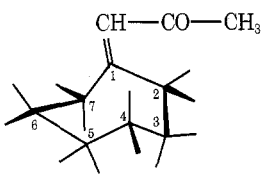


23a, $n = 1$
b, $n = 2$
c, $n = 3$

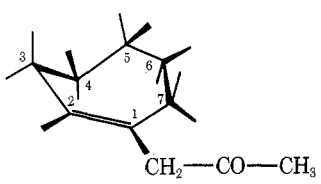


24

The acid-catalyzed equilibria between α,β- and β,γ-unsaturated ketones in a series of 4-alkylcyclohexenones has been investigated by Lewis and Williams.[24] With no 4-alkyl substituent, essentially no β,γ isomer is present at equilibrium. The percentage of β,γ isomer varies from 30% for methyl and ethyl, 40% for isopropyl, to 50% for *tert*-butyl. This is, of course, opposite to the order expected from hyperconjugation effects, and was explained in terms of the absence of any significant steric interaction between the alkyl group and ring hydrogens in the β,γ isomer in its nonflexible flattened boat



21c



22c

Table I. Equilibria under Acidic Conditions[a]

α,β	β,γ	ΔG°
2a >99%	**3a** <1%	
2b >99%	**3b** <1%	
2c >99%	**3c** <1%	
4a 92%	**5a** 8%	+1.5
4b 96%	**5b** 4%	+1.9
4c 96%	**5c** 4%	+1.9
8b 44%	**9b** 50%	−0.14

[a] ΔG° values in kcal/mol. All experiments carried out in light.

conformation, and the presence of such an interaction in the α,β isomer.

Results

The unsaturated ketones **2a**, **2b**, **2c**, **4a**, **4b**, **4c**, and **8a**, **8b**, **8c** were prepared as previously described[1] by cyclization of the appropriate dione. As obtained from the syntheses, all ketones contained varying but significant (usually 20% or more) amounts of the corresponding β,γ-unsaturated ketones **3**, **5**, and **9**.

It has been found[25] that α,β- and β,γ-unsaturated ketones have a tendency to reequilibrate on attempted distillation, possibly due to the glass having sufficient basic or acidic properties (depending on its previous treatment) to catalyze the equilibration. Gas chromatography on a Carbowax column was chosen as the most convenient analytical technique. It was, however, essential to show that equilibration did not occur in the injection port or on the column. Details of the GLC procedures and precautions are given in the Experimental Section.

For equilibration studies, the procedure adopted for each pair of compounds was as follows. Small quantities of pure α,β-unsaturated and pure β,γ-unsaturated isomers were obtained by preparative GLC. These were separately dissolved in methanol and stirred with HCl at room temperature until no further changes in isomer ratios could be observed on the GLC. A maximum of about 18 h was required. The isomer ratios obtained by measurement of the area under each peak proved to be identical in each equilibration within the limits of measurement error. These results are shown in Table I.

We also attempted to study the isomer mixtures arising from kinetic protonation of the enolate ion, formed using potassium *tert*-butoxide in *tert*-butyl alcohol, with dilute acetic acid after the method of House et al.[26,27] As can be seen from Table II, we obtained results identical within experimental error with those obtained by equilibration with HCl, leading us to believe that the conditions we were using did not prevent isomerism subsequent to protonation, or were achieving protonation on oxygen to give the enol, which was tautomerizing to the equilibrium mixture. In the case of **2b**, for which House[26] reported a mixture of 15% **2b**, 30% **3b**, and 55% **24** by NMR analysis, we repeated the experiment several times (increasing the concentration of base, using more dilute acetic acid, etc.), but could not detect any of the isomer **24**. We have not yet pursued these experiments further. It should be noted that we did not distill our products and that our experiments were on a much smaller scale.

In order to gain some insight into the relative stability of the double bond in ketones **4** and **5**, we subjected the alkenes **6** and **23** equilibration with *p*-toluenesulfonic acid in benzene, under reflux initially to hasten the attainment of the equilibrium. The alkenes **23** required to approach the equilibrium from that side were obtained by preparative GLC from the mixtures produced by acid treatment of the alkenes **6**. The results are shown in Table III.

Table II. Product Mixtures Observed on Protonation of Enolate Ions[a]

α,β	Registry no.	β,γ	Registry no.	ΔG°
2a >99%	1489-28-7	**3a** <1%	14661-63-3	
2b >99%	1196-55-0	**3b** <1%	13837-12-2	
2c >99%	19198-29-9	**3c** <1%	59562-88-8	
4a 93%	59562-89-9	**5a** 7%	59562-92-4	+1.5
4b 96%	59562-90-2	**5b** 4%	59562-93-5	+1.9
4c 96%	59562-91-3	**5c** 4%	59562-94-6	+1.9
8a 67%	59562-95-7	**9a** 33%	59562-98-0	+0.42
8b 44%	59562-96-8	**9b** 56%	59562-99-1	−0.14
8c 41%	59562-97-0	**9c** 59%	59563-00-7	−0.22

[a] ΔG° values in kcal/mol. All experiments carried out in light.

Table III. Equilibration of Alkenes[a]

Compd with exocyclic double bond	Compd without exocyclic double bond	ΔG°	Registry no. 6	Registry no. 23
6a 54%	**23a** 46%	+0.1	59563-01-8	59563-04-1
6b 17%	**23b** 83%	−0.9	59563-02-9	59563-05-2
6c 42%	**23c** 58%	−0.2	59563-03-0	59563-06-3

[a] ΔG° values in kcal/mol.

Discussion

It can be seen from Table I that, although the α,β-unsaturated isomer remains favored by a substantial energy difference, alkylation in the α position *decreases* the percentage of α,β-unsaturated isomer at equilibrium. However, the percentage of α,β-unsaturated isomers **2** and **4** is, in each case, higher than most of the examples discussed in the introduction. Ketones **2/3** can be considered as β,γ dialkylated and ketones **4/5** as α,β,γ trialkylated. It must be remembered, however, that is is the differences between the α,β and β,γ isomers rather than the actual substitution pattern which is important unless the hyperconjugative factors override the steric interactions. In the light of the data presented in the introductory discussion, this appears unlikely. An examination of models reveals that in the β,γ isomer, there is an eclipsed 1,3 interaction between the quasi-equatorial hydrogen or methyl group on the α carbon and the quasi-equatorial hydrogen on the nearest allylic carbon (H_γ in **3** and **5**). This interaction is much less—it is staggered—in the α,β isomer, and may be the major difference. The interaction is more severe in the alkylated ketones **5**, so that the greater percentage of β,γ isomer in those cases may reflect the hyperconjugative effect of the alkyl group, only partly counteracted by the added steric interaction.

The six-membered ring can be expected to adopt at least approximately the same conformation in all the α,β-unsaturated isomers, because of the planar nature of the conjugated system. The β,γ isomers appear, from models, to each have a similar flattened boat conformation.[23] Thus, the differences between the equilibria in **4a/5a**, **4b/5b**, and **4c/5c** should reflect the conformational effects of the other ring. It is seen that the observed results do not parallel those of Kon in the cycloalkylidene methyl ketones **21**. Our results with the alkenes **6** and **23** (Table III) indicate that there are significant differences in the relative stabilities of the double bonds as the ring size varies. Interestingly, these results do closely parallel those in the cycloalkylidene methyl ketone series.

It seems clear that the equilibria between α,β- and β,γ-unsaturated ketones, particularly in cyclic compounds, are

subject to conformational and hyperconjugation effects, as well as the more commonly appreciated resonance stabilization of the α,β isomer. It clearly is wrong to always assume that the α,β isomer will predominate.

The difference between the reported[26] 97% α,β- and 3% β,γ-unsaturated isomer for equilibration of **2b/3b** using 5% aqueous HCl in ethanol and our results (>99 and <1%, respectively) in almost anhydrous methanol probably reflects the greater polarity of the alcohol/water solvent. The conjugation present in the α,β-unsaturated isomer presumably serves to disperse the charge on the carbon of the carbonyl, marking that isomer more preferred in a less polar solvent.

The equilibrium between ketones **8** and **9** (Table II) showed much higher percentages of β,γ-unsaturated isomer at equilibrium. It appears that the two isomers were of comparable thermodynamic stabilities. However, the equilibration of **8b** appeared to involve a photochemical effect,[28] for, after several hours in the dark, the mixture contained less than 5% of the β,γ-unsaturated isomer **9b**. The quantities of ketones **8a**, **8b**, and **8c** available were not sufficient for a thorough investigation. We are pursuing this aspect with more readily accessible compounds containing the appropriate structural elements.

Experimental Section[29]

Typical Equilibration Procedure. Samples of pure α,β- and β,γ-unsaturated isomers were collected by preparative GLC. This was often done in conjunction with the collection of these isomers for spectral determinations and analyses.[1] In the course of these collections, other components were present and collected.[30] The pure α,β- and β,γ-unsaturated isomers (ca. 100 mg) were separately dissolved in ethanol, and a few drops of concentrated HCl added. The mixtures were stirred at 25 °C and the equilibrations allowed to continue until no further change was observed in either reaction, at which time the mixtures were carefully analyzed by measurement of the areas of GLC peaks. If necessary, the reaction was continued until the ratio of components was the same in both reactions. The equilibrations generally took less than 18 h.

Typical Enolate Ion Formation and Protonation.[26] Samples of α,β- and β,γ-unsaturated isomers were collected as above. Samples, ca. 100 mg, were added to a solution of 10 equiv of potassium *tert*-butoxide in ca. 10 ml of *tert*-butyl alcohol and the mixture stirred for at least 2 h. The mixture was poured into ca. 50 ml of cold 10% aqueous acetic acid. The solution was extracted with ether, and the ethereal extract washed with sodium bicarbonate, dried over $MgSO_4$, and evaporated to small bulk. The product was then examined by GLC.

Since this enolate protonation did not give the results reported[26] by House for ketones **2b**, the experiment was repeated several times, increasing and decreasing the concentration of both the base and the quenching acetic acid, but no difference in the ratio of products was observed.

Alkene Equilibration Procedure. For each series, samples of the alkenes **6** and **23** were obtained pure by preparative GLC on a Carbowax column. Samples (ca. 100 mg) of each were separately dissolved in benzene (ca. 10 ml) with a tenfold excess of *p*-toluenesulfonic acid. The mixtures were refluxed overnight or until no further change was observed in the isomer ratios, determined by GLC. The mixtures were then allowed to stand at room temperatures for 2–3 h before the final GLC analyses were performed. In each case, the ratio of isomers was the same in both experiments.

GLC Precautions. In every case, the pure α,β- and β,γ-unsaturated isomers were separately collected as they emerged from the GLC detector. Reinjection of each collected isomer gave only one peak at the same retention time as before, verifying that no detectable isomerization was occurring in the GLC system.

In order to make use of the method of internal normalization[31] for analysis, it was then necessary to ascertain that no selective irreversible retention was occurring. This was done by taking a mixture of the α,β- and β,γ-unsaturated isomers **2b** and **3b**, and determining the ratio of the areas under the peaks. The GLC conditions were then altered by increasing the temperature and carrier gas flow rates so that the isomers were no longer separated. The mixture was collected as it came off the chromatograph, the former GLC conditions were restored, and a sample reinjected. The ratio of the areas under the peaks was determined to be the same within normal measurement error. Furthermore, a 1-μl sample of pure isomers gave peak areas within 10% of that given by 1 μl of an α-decalone, a structurally similar ketone (but not an unsaturated ketone).

The possibility that one of the supposed pure isomers contained some other double bond isomer of identical retention time was ruled out by the spectra of the isomers as collected from the GLC. Any such other isomer would contain a vinyl hydrogen. Ketones **3**, **4**, and **5** showed[1] no vinyl hydrogen signal in the NMR. Ketones **2** showed[1] only one vinyl proton in the NMR and showed[1] no nonconjugated ketone in the ir.

The alkenes **6** and **23** were also purified in similar manner. Although small amounts of other double bond isomers were clearly formed in the preparation of these alkenes **6**, only **6** and **23** were observed on equilibrating pure samples of each with acid. The absence[1] of any vinyl signals in the NMR confirmed that this was so. The absence of any selective irreversible retention was verified as above.

In view of the extreme similarity of the compounds—identical molecular formula, virtually identical functional groups—differences in response to the thermal conductivity detector were assumed negligible. The reproducibility of the GLC analyses was ±1%, although the overall uncertainty in the results may be somewhat higher.

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(30) Diethylated compounds were specifically identified by the presence of a molecular ion at 28 amu higher than the corresponding monoethylated compound. Small quantities of the dialkylated products were detected in the product mixtures from which the following ketones were isolated for equilibrium studies: **8a/9a**, **8b/9b**, **8c/9c**. Product mixtures used for isolation of ketones **4** and **5** had been freed of dialkylated impurities by spinning band distillation.
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