Synthesis of δ-cyclohexyl- and δ,δ-alkylene-α,α-dicarbonyl-substituted dienes and study of their valence isomerization

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β-Cyclohexylacrolein, β-cyclohexylmethacrolein, or α-cycloalkylidenalkanal were condensed with methyl acetoacetate or dimethyl malonate to give the δ-cyclohexyl- and δ,δ-alkylene-substituted α,α-dicarbonyl-containing α,β,γ,δ-dienes. The structures of the reaction products were studied using 1H NMR, 13C NMR, and UV spectroscopy. The diene keto esters bearing no substituents at the γ-position were shown to be in fact three-component equilibrium mixtures comprised of E- and Z-isomers of the diene (at the α,β bond) and a corresponding 2H-pyran. On the other hand, for keto esters with a Me group at the γ-position the equilibrium is shifted entirely to the 2H-pyran. In contrast with the keto esters, dienic diesters exist only in the open form.

Key words: β-cyclohexylpropanals and α-cycloalkylidenalkanals; Knoevenagel condensation; α,β,γ,δ-dienones; 2H-pyrans; valence isomerization; effect of γ-substituents.

This work is devoted to further study of dienone (D) \( \rightarrow \) 2H-pyran (P) valence isomerization.

Earlier,1–5 we discovered a considerable influence of substituents introduced into the dienone molecule, especially at the γ-position, on their ability for valence isomerization into corresponding 2H-pyran, which allowed solvato-, thermo-, and photochromic properties to be exhibited by some dienones. The influence of δ-substituents remained poorly known owing to the absence of corresponding dienones.

δ-Cyclohexyl- and δ,δ-alkylene-α,α-dicarbonyl-containing dienes previously unknown were synthesized with the aim to study the influence of δ-substituents on valence isomerization:

Knoevenagel condensation between methyl acetoacetate (1) or malonate (2) and α,β-unsaturated aldehydes (3)—(7) was used to obtain these dienes:

![Diagram](image)

3–4

5–7

3: \( R = H, \) 5, 6: \( n = 1; R = H (5); R = Me (6); \)

4: \( R = Me; \) 7: \( n = 0, R = H \)

Aldehydes 3 and 4 were obtained via the oxy-propenylation of cyclohexylmagnesium bromide with (trimethylsilyloxy)acroleins following an earlier described procedure.6

Aldehydes 5 and 6 were synthesized from 1,1-diethoxycyclohexane (8) via acetal-alkoxyalkene condensation through intermediates 9–12.6

The synthesis of compound 9 was described earlier; however, we found that when using FeCl3, recommended as the best catalyst in the work, the yields of compound 9 were no more than 10%. The best yields of compounds 9 and 10 (76 and 61%, respectively) were obtained when BF3·OEt2 was used as catalyst.

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The transformation of compound 10 to diene 12 was carried out in a 49% yield with the use of the procedure described in the work for diene 11, but at a higher temperature than for the latter. The hydrolysis of dienes 11 and 12 in the presence of phosphoric acid resulted in aldehydes 5 and 6 in 25 and 75% yields, respectively.

Condensation of aldehydes 3–7 with esters 1 and 2, resulting in dicarbonyl-containing dienes (13–21), was carried out in the presence of piperidine or a mixture of piperidine and glacial AcOH, a part of the initial components being recovered unchanged. The reaction conditions and the substances thereby obtained which were isolated by vacuum distillation are given in Table 1; their structures were determined using UV spectra (Table 1) and \(^1\)H and \(^13\)C NMR (Tables 2 and 3). It follows from these data that diene ketoesters 13, 17, and 20 are equilibrium mixtures of dienones D(E) and D(Z) and 2H-pyran P.

Three sets of resonance signals of these compounds are observed in \(^13\)C and \(^1\)H NMR spectra. The signals were referred to the diene or 2H-pyran forms on the basis of a comparison of chemical shift and coupling constant values of compounds 13, 17, and 20 with that of dienones and 2H-pyran, studied earlier. Referring the signals to E- and Z-isomers in ketoester 13, 17, and 20, obtained from ester 1 and aldehydes 3, 5, and 7, are equilibrium mixtures of E- and Z-isomers at a \(\alpha,\beta\)-double diene bond, D(E) and D(Z), and a corresponding 2H-pyran P.

In accordance with our data concerning stereospecificity of chemical shifts for \(^13\)C atoms of carbonyl groups in conjugated carbonyl-containing compounds the signals were referred to E- and Z-isomers in ketoesters 17 and 20: \(\delta\) 200.77 and 200.67 in E-isomer and \(\delta\) 195.17 and 195.30 in Z-isomer. It follows from the NMR data of E- and Z-isomers of ketoesters 13, 17, and 20 (\(J_{\beta,\gamma} = 12–12.5\) Hz) that S-trans conformation is realized there.

From the results of the study of temperature dependence of the isomeric composition of \(\alpha,\alpha\)-dicarbonyl-containing dienes investigated earlier, it follows that compounds 13, 17, and 20 are also equilibrium mixtures of dienes D(E), D(Z) and 2H-pyran (P).

Condensation products of ketoester 1 with aldehydes 4 and 6 are substituted 2H-pyrons 15 and 19. There is one set of resonance signals referred to 2H-pyrons in \(^1\)H and \(^13\)C NMR spectra of compounds 15 and 19. This referring is confirmed by UV spectra data as well (Table 1) because the most intense absorption band in the spectra of these compounds is found in a short-wave range: 207 nm (15) and 208 nm (19), which is consistent with UV spectra data of 2H-pyran obtained earlier.

Diene diesters 14, 16, 18, and 21 were obtained by reaction of dimethyl malonate 2 with aldehydes 3, 4, 5, and 7. According to \(^13\)C and \(^1\)H NMR spectra data they exist only in the open form and do not contain 2H-pyran.

Diesters 14, 18, and 21 exist in the form of S-trans-conformers \(J_{\beta,\gamma} = 12–12.5\) Hz; diester 14 has a trans-position of protons at the \(\gamma,\delta\)-bond \(J_{\gamma,\delta} = 15\) Hz. There is one absorption maximum within the 274–294 nm range in UV spectra of diesters 14, 16, 18, and 21, which is characteristic of diene diesters.

It should be noted that a pyran form is also not observed for either diene diester synthesized earlier, which contain a Me, Ph, or NMe\(_2\) group at the \(\delta\)-position.

The percentage of valence isomers in a D(E) – P equilibrium mixture of keto esters 13, 17, and 20 in CDCl\(_3\) is given in Table 1. The data from this Table show that the most displacement of equilibrium to 2H-pyran is observed in keto ester 17, that is probably connected with the destabilization of dienone due to steric hindrance caused by pentamethylene group.

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* Compound 12 seems to be a mixture of dienes with R\(^1\) = Me and R\(^1\) = Et.

** Content of valence isomers in CD\(_3\)OD is the same.