

STEREOISOMERISM IN 2-BENZALCYCLANONES¹

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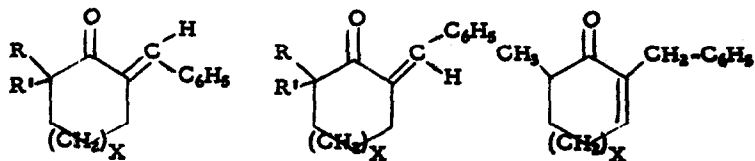
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The base catalyzed aldol condensation of cyclanones with benzaldehyde is a well known reaction and leads to products to which the structure of trans-2-benzalcyclanones, e. g. I, has been ascribed.^{3,4} Cornubert and coworkers³ assigned the structure of cis-2-benzalcyclanones, e. g. IV, to isomeric products resulting from acid catalyzed aldol condensation of several cyclanones with benzaldehyde. Previous work with benzalcyclanones^{4,5} made this structure assignment doubtful. Reinvestigation of this problem showed that the compound obtained in the acid catalyzed aldol condensation of 2-methylcyclohexanone or upon isomerization of I (λ_{\max} 284 μ ; ϵ 16,000) with acid actually possesses structure VI (λ_{\max} 234 μ ; ϵ 9,000). Thus 2-benzyl-6-methyl-2-cyclohexenone (VI) upon ozonolysis yielded phenyl acetic and α -methyl glutaric acid. Sodium borohydride reduction of VI gave 2-benzyl-6-methyl-2-cyclohexenol reconvertible to VI with manganese dioxide but devoid of conjugative absorption in the ultra-violet. Ketone I, on the other hand, is reduced to 2-benzal-6-methyl-cyclohexanol (VIII) that absorbs at 244 μ ; ϵ 19,000.

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- 1 We are grateful to the National Institutes of Health for financial support of this work (Grant CY-4474).
 - 2 Shell Oil Company Fellow 1960-61.
 - 3 R. Cornubert, Bull. Soc. Chim. Fr. (5) 5, 513 (1938)
 - 4 A. Hassner and N. H. Cromwell, J. Amer. Chem. Soc. 80, 893 (1958)
 - 5 H. W. Wanzlick and W. Menz, Chem. Ber. 87, 475 (1954)

It is noteworthy that these isomerizations proceed from the more to the less conjugated system and in five as well as in six-membered rings. Thus trans-2-benzal-5-methylcyclopentanone (III) is converted by acid to



- I X=1, R=CH₃, R'=H IV X=1, R=CH₃, R'=H VI X=1
 II X=1, R=R'=C₆H₅ V X=1, R=R'=C₆H₅ VII X=0
 III X=0, R=CH₃, R'=H

its endocyclic unsaturated isomer VII. 6,6-Disubstituted-2-benzalcylohexanones however are not isomerized under these conditions.

IV and V, the actual cis isomers of benzalketones I and II,⁶ were obtained in good yield by light irradiation of solutions of I and II respectively. IV (λ_{\max} 270 $m\mu$; ϵ 6,700) is converted by heat into I and by treatment with acid into VI. The infrared spectra of cis benzal ketones IV and V indicate steric inhibition of orbital overlap ($\nu_{C=O}$ 1690 cm^{-1} , intensity ratio $\frac{\nu_{C=C}}{\nu_{C=O}} = 0.2-0.3$) with respect to the spectra of the trans isomers ($\nu_{C=O}$ 1668 cm^{-1} , intensity ratio $\frac{\nu_{C=C}}{\nu_{C=O}} = 1$).

⁶ The trans isomer III, reported by J. P. Collman, *J. Org. Chem.* **26**, 3162 (1961) to absorb at 270 $m\mu$ actually absorbs at 292 $m\mu$ but converts readily to the cis isomer VI which absorbs at 268 $m\mu$.