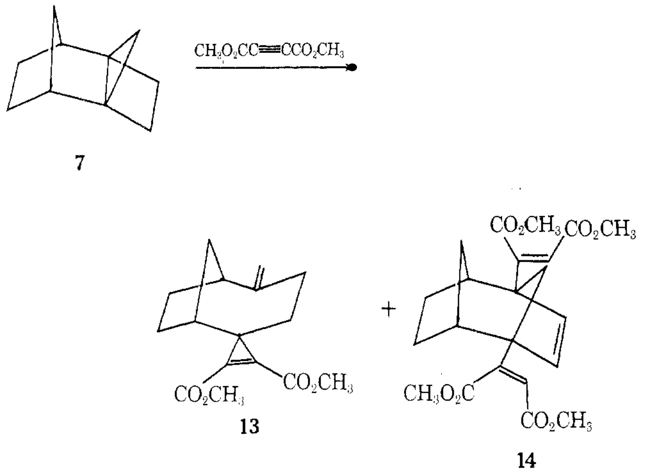

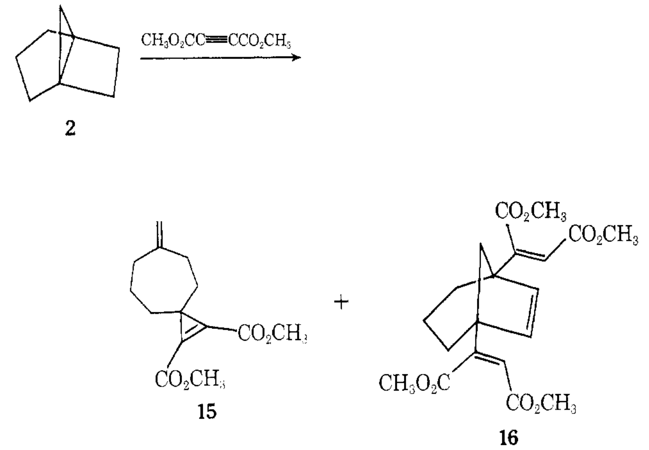

DMAD) the ratio of 13 to 14 is 3:2, but the less strained propellane 2 gives less of the cyclopropene product. The ratio of 15 to 16 in carbon tetrachloride (1 *M* DMAD) is 1:7. The ratio of 13 to 14 increases with increasing solvent polarity, but is not sensitive to changes in the concentration of DMAD. Thus a simple mechanism based on partitioning of a 1:1 intermediate diradical between 13 and 14 can be eliminated. Investigation of other mechanistic possibilities is underway.

Supplementary Material Available. Full nmr data for compounds 7, 8, 11, 12, 13, 14, 15 and 16 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-2315.

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(1) Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(10) See K. B. Wiberg, K. C. Bishop, III, and R. B. Davidson, *Tetrahedron Lett.*, 3169 (1973), for a discussion of cases where reactivity toward electrophiles does not always parallel the relief of strain energy.

(11) The strain energy of the ring system for **11** and **12** has been calculated to be $\sim$40 kcal/mol: E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8005 (1973).

(12) The structures of these products are supported by characteristic spectral data. The position of the double bond in **14** was established by using *exo*-3,4-dideuterio-**7**.

(13) See P. G. Gassman, *Accounts Chem. Res.*, **4**, 128 (1971).

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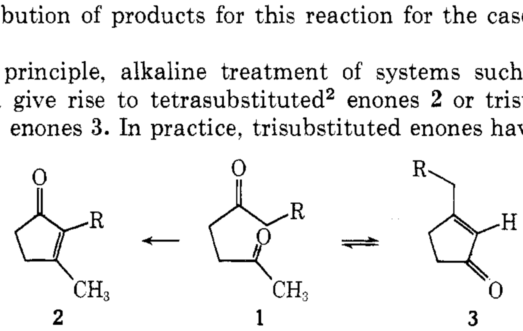
Cyclenones. V.[1] Mechanistic Factors in the Aldol Cyclization of 2,5-Alkanediones

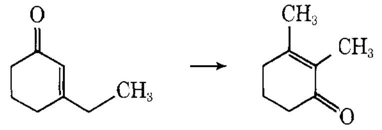
Summary: The cyclization of 6-alkyl-2,5-hexanediones (1) in aqueous ethanolic base is a kinetically controlled reaction, with the major product being the 2-alkyl-3-methylcyclopent-2-enones (2).

Sir: The intramolecular aldol condensation is an important pathway for the synthesis of cyclenones. We have been studying those factors which influence the direction of cyclization of unsymmetrical diketones of the type $RCH_2CO(CH_2)_nCOCH_3$. In this, and in the accompanying communication, we wish to report the first definition of some of the kinetic *vs.* thermodynamic influences on the distribution of products for this reaction for the case $n = 2$.

In principle, alkaline treatment of systems such as 1 could give rise to tetrasubstituted[2] enones 2 or trisubstituted enones 3. In practice, trisubstituted enones have not been reported[3] from such a reaction in the cyclopentenone[4] series. Reported failure to obtain products of general formula 3 can be explained by either of two hypotheses: (A) the tetrasubstituted enone 2 is the thermodynamically more stable cyclopentenone and that under the reaction conditions the formation of the trisubstituted product 3 is reversible; or (B) the reaction is kinetically controlled and compounds of type 3 are not formed at all under these conditions.



The reported[5] isomerization of 3-ethylcyclohex-2-enone (4) to a 93:7 mixture of 2,3-dimethylcyclohexenone and 4, by refluxing for 3 hr with 5% sodium hydroxide, lent some credence to hypothesis A.



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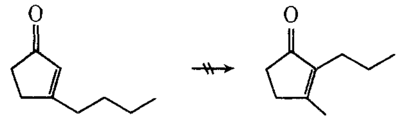
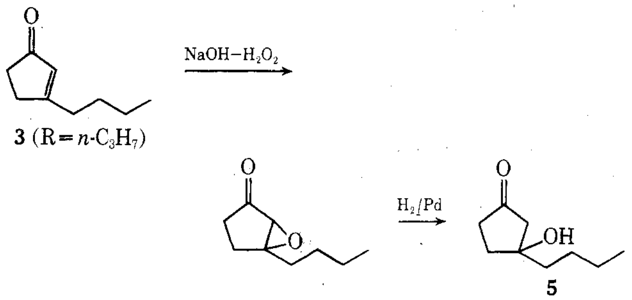
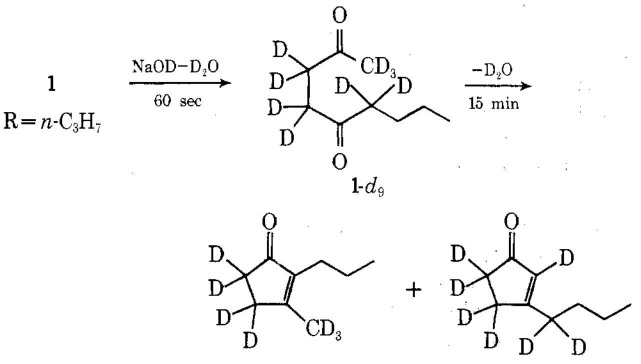
To test the degree of control over the reaction in the case of cyclopentenones, we have prepared 3-n-butylcyclopentenone[6] (**3**, R = $n\text{-}C_3H_7$) as a representative 3-n-alkylcyclopentenone and submitted it to reaction conditions (2% NaOH-EtOH-H_2O, reflux) which serve to convert **1** → **2** (R = $n\text{-}C_3H_7$).

Interestingly, the trisubstituted enone was recovered in high yield[7] (>95% distilled), and we were unable to detect the presence of the tetrasubstituted enone **2** which is characterized by a sharp resonance (250-MHz nmr spectrum) at δ 2.040 for the vinyl methyl group. Lacey's conditions[5a] were also not useful[8] for the conversion of **3** → **2**. Aldol **5**, prepared in 93% yield by catalytic hydrogenation[9] of the corresponding epoxy ketone derived from 3-n-butylcyclopentenone, was submitted to the cyclization conditions, and the sole detectable product was compound **3** (R = $n\text{-}C_3H_7$). Thus, at least in this case, to the extent that the aldolization of **1** → **5** had occurred, the trisubstituted product, **3**, would have been obtained. Under identical reaction conditions the corresponding 2,5 diketone (**1**, R = $n\text{-}C_3H_7$)[10] cyclized in excellent yield (15 min at 90°, 97%) to a 94:6 mixture of **2** and **3** (R = $n\text{-}C_3H_7$). This represents the first documented case in which a trisubstituted enone is formed as a minor product from the cyclodehydration of a compound of general formula **1**. When the same reaction was carried out in a deuterated solvent system and quenched after 1 min, 1-d_9 (R = $n\text{-}C_3H_7$) was recovered in >95% yield. The exchangeability of all nine acidic α hydrogens with recovery of starting diketone convincingly shows that enolate formation is reversible, and cannot be construed as the product determining step. We are thus obliged to conclude that, under the reaction conditions thus far employed, the reaction in question is kinetically controlled at the level of aldol step and that the transition state for cyclization of enolate **6** is approximately 2.0 kcal/mol more stable than that for **7**.


3 (R = n-propyl) 2 (R = n-propyl)

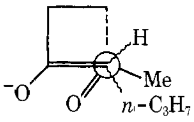

3 (R = $n\text{-}C_3H_7$)

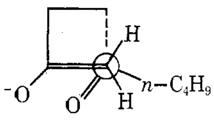
5


1 R = $n\text{-}C_3H_7$

1-d_9

2-d_7, 94% 3-d_7, 6%


6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(6) The synthesis of this and related 3-alkylcyclopentenones is reported in the following communication.

(7) The tetrasubstituted cyclopentenone **2** (R = $n\text{-}C_3H_7$) was also stable to these conditions.

(8) We never observed more than 5% conversion under Lacey's conditions. These reactions always led to significant loss of material.

(9) *Cf.* D. P. Strike and H. Smith, *Tetrahedron Lett.*, 4393 (1970).

(10) Prepared by the low temperature (−78°) addition of butyllithium to the ethylene ketal of ethyl levulinate, followed by acid hydrolysis.

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Cyclenones. VI.[1] The Retroaldol-Aldol Route to *cis*-Jasmone and Related Compounds

Summary: When 3-alkylmethylcyclopent-2-enones (3) synthesized in two steps from cyclopentenone are heated with *aqueous* base, they are converted to 2-alkyl-3-methylcyclopent-2-enones.

Sir: In the preceding communication,[1] we have demonstrated that the cyclization of 2,5-nonanedione (**1a**) in aqueous alcoholic base is irreversible; *i.e.*, the products **2a** and **3a** are stable to the conditions of their formation. We now wish to report a two-step synthesis of **3a** and related 3-alkylmethylcyclopentenones **3b**–**3d**. Concurrently we wish to report conditions which are successful in effecting their isomerizations to the tetrasubstituted enones **2a** (**2**, R = $n\text{-}C_3H_7$), **2b** (dihydrocinerone), **2c** (dihydrojasmone), and **2d** (*cis*-jasmone), respectively.