tional transformation in a large ring is asymmetric.[9,10] Models show that a corner and adjacent noncorner carbon atom (*e.g.*, A and B in I) can be moved so that the dihedral angle ω changes sign, with other dihedral angles undergoing the minimum possible change. Similar or identical steps can be carried out successively at the remaining three corner positions.[11] The end result is a mirror-image conformation of I, and the cmr results are consistent with such a process and show that the free-energy barrier is 7.3 kcal/mol.

Cyclotetradecane is thought to be conformationally homogeneous and to have the "rectangular" diamond lattice conformation II,[12] which has four different carbons in the ratio 2:2:2:1. The cmr spectrum at −132° shows lines of approximately 4:1:2 intensity ratio, in agreement with II, provided that two of the different carbons in II have such a small chemical-shift difference that they are not resolved. Pseudorotation[10] of II can proceed by a process analogous to that given for cyclododecane, with opposite corner (C) positions being involved in two successive steps.[13]

Pseudorotation of the type described here for the C_{10}, C_{12}, or C_{14} hydrocarbon results in all the carbons exhibiting a single chemical shift, and the same effect also holds for the protons. Thus, only a single conformational process can be detected in each compound by nmr.

Spectra of the odd-numbered cycloalkanes (n = 11, 13, and 15) remained sharp down to at least −135°. Some broadening occurred a lower temperatures, but separation into more than one peak was not observed. Further work on these compounds is in progress.

Acknowledgments. This work was supported by the National Science Foundation and the U. S. Public Health Service.

[9] H. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7047 (1967).

[10] Semiquantitative calculations by J. Dale, University of Oslo, show that relatively large conformational barriers should be present in the C_{12} and C_{14} cycloalkanes and a much smaller barrier in cyclodecane. (We are most grateful to Professor Dale for sending us copies of manuscripts on this and related topics.)

[11] The overall process is similar to pseudorotation in the cyclooctane boat-chair[2,9] or in the cyclodecane boat-chair-boat (J. D. Dunitz, *Pure Appl. Chem.*, **25**, 495 (1971)).

[12] G. Borgen and J. Dale, *Chem. Commun.*, 1340 (1970).

[13] Line-shape studies in this system are in progress. The present results show that $\Delta G^{\ddagger}$ for cyclotetradecane from the cmr spectra is about 7 kcal/mol at −115°.

F. A. L. Anet,* A. K. Cheng, J. J. Wagner
Contribution No. 3036, Department of Chemistry
University of California, Los Angeles, California 90024

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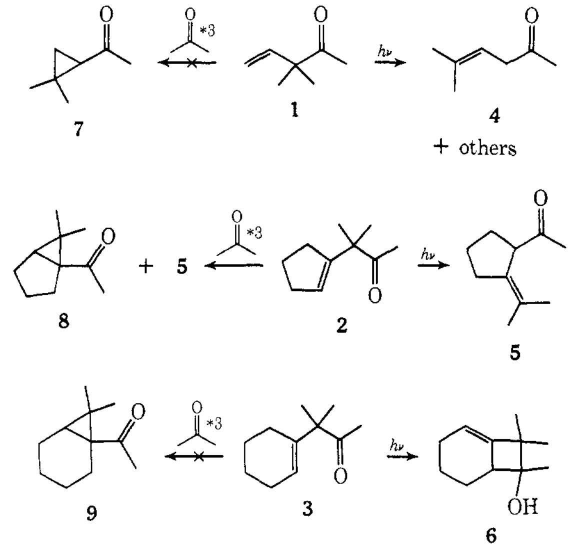
Effect of Ring Size on the Photochemical Behavior of β,γ-Unsaturated Ketones

Sir:

Although β,γ-unsaturated ketones are capable of a variety of photochemical reactions, it is not yet clear what structural features determine the pathway which they will follow.[1] The results reported here demonstrate the delicate balance between acyl shift and γ-hydrogen abstraction in the singlet and show that the triplet behavior of these compounds is strongly affected by the degree to which the double bond is sterically constrained.

We have prepared the closely related compounds **1–3** by reaction of methyllithium with the appropriate carboxylic acid.[2] Scheme I shows the results of irradiating them in benzene at 313 nm and in acetone as triplet sensitizer and solvent. The products **4**, **5**, and **6** were isolated by preparative vpc and their structure determined by nmr and ir spectroscopy: **4**, δ 1.70 (br d, 6 H), 2.01 (s, 3 H), 2.99 (br d, 2 H), 5.24 (br m, 1 H); ir 1719 cm^{-1} (C═O); **5**, 1.65 (br d, isopropylidene), 2.00 (s, methyl ketone), 1.7–2.4 (m, ring protons), 3.37 (br s, methine); ir 1710 cm^{-1} (C═O); **6**, 0.97 (s), 1.16 (s), 1.19 (s) (methyls), 1.3–2.2 (m, ring protons), 5.27 (m, olefin); ir (CCl_4) 3600 cm^{-1} (free OH), 1380 (d, *gem*-dimethyl). Compound **7** was prepared from dimethyloxosulfonium methylide and mesityl oxide;[3] no trace of this material could be detected by gas chromatography at 125° of irradiated acetone solutions of **1**. Compound **8** was synthesized independently by photolysis of the pyrazoline[4] from 2-diazopropane and acetylcyclopentene. Its spectral properties were: nmr (CCl_4) δ 1.00 (s), 1.08 (s) (methyls), 1.5–2.1 (m, ring protons); ir 1692 cm^{-1} (C═O).

Scheme I



Looking first at the singlet-state photochemistry of **1–3**, one notes that while **1** and **2** undergo an apparent 1,3-acyl shift, **3** proceeds *via* γ-hydrogen abstraction to cyclobutanol **6**. Inspection of molecular models suggests a reason for the difference between **2** and **3**: the much greater distance between the γ hydrogen and the carbonyl oxygen in **2** precludes γ-hydrogen abstraction,[5] leaving acyl shift as a last resort. Although formation of cyclobutanols from β,γ-unsaturated ketones has good precedent,[6] acyl cleavage is a com-

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[1] See R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957 (1971), and references cited therein.

[2] D. B. Bigley and R. W. May, *J. Chem. Soc. B*, 557 (1967).

[3] R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967).

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[5] N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Shore, *Accounts Chem. Res.*, **5**, 92 (1972).

[6] (a) N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, 3671 (1966); (b) E. F. Kiefer and D. A. Carlson, *ibid.*, 1617 (1967); (c) R. C. Cookson, J. Hudec, G. E. Usher, and A. Szabo, *Tetrahedron*, **24**, 4353 (1968); (d) R. C. Cookson and N. R. Rogers, *J. Chem. Soc., Chem Commun.*, 809 (1972); (e) J. C. Dalton, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972, ORGN 97.

peting process in acylic systems. In the present case, **6** is virtually the only volatile product from **3**, suggesting the existence of a fundamental difference between cyclic and acyclic systems. A further manifestation of this difference is the formation of the α-cleavage products biacetyl and dimethylallyl radical dimers[7] from **1** but not from **2**. The absence of expected α-cleavage products in cyclic systems is difficult to rationalize but may be related to ground-state conformational effects,[8] or stability of the incipient allylic radicals.[9]

The triplet-sensitized reactions of **1–3** also exhibit a striking dependence on structure. As shown in Scheme I and in Table I, the triplet state of compounds **1** and **3** is essentially inert while **2** proceeds in part to the oxadi-π-methane product **8**. These results support the idea[10] that more flexible double bonds allow the excited molecule to lose energy by twisting. In monocyclic systems, we may place the lower limit of rigidity necessary for reasonably efficient oxadi-π-methane reaction at a five-membered ring, in complete accord with previous results.[11] The inertness of **3** is reminiscent of 1-acetylcyclohexene, which is too flexible to photodimerize.[14] Two recent reports[15,16] indicate that the oxadi-π-methane reaction will occur in systems having an acyclic double bond. In each case, the reaction is very slow and the products could be separated from acetone photolysis products[17] only by virtue of their considerably higher molecular weight. The formation of **5** in the acetone-sensitized irradiation of **2** was unexpected. Although a number of trivial explanations can be devised for its presence, the outcome of several control experiments convinces us that the conversion of **2** to **5** is an unprecedented triplet 1,3-acyl shift. In particular, vpc analysis during irradiation of **2**, even at −78°, reveals that **5** and **8** build up at the same rate.

Table I. Quantum Yields for β,γ-Unsaturated Ketones[a]

	Direct[b]		Sensitized[c]	
Ketone	$\Phi_{-k}{}^{d}$	$\Phi_{p}{}^{e}$	$\Phi_{-k}{}^{d}$	$\Phi_{p}{}^{e}$
1	0.68	**4**, 0.15	<0.04	
2	0.33	**5**, 0.04	0.21	**5**, 0.038; **8**, 0.013
3	0.24	**6**, 0.10	0.009	

[a] At 25° and 313 nm, measured by vpc peak areas. [b] In benzene. [c] In acetone. [d] Disappearance of starting ketone. [e] Formation of specified product. Low values for **2** are due to photochemical formation of nonvolatile products or to thermal destruction of volatile photoproducts. Tlc of irradiated solutions showed a spot remaining at the origin.

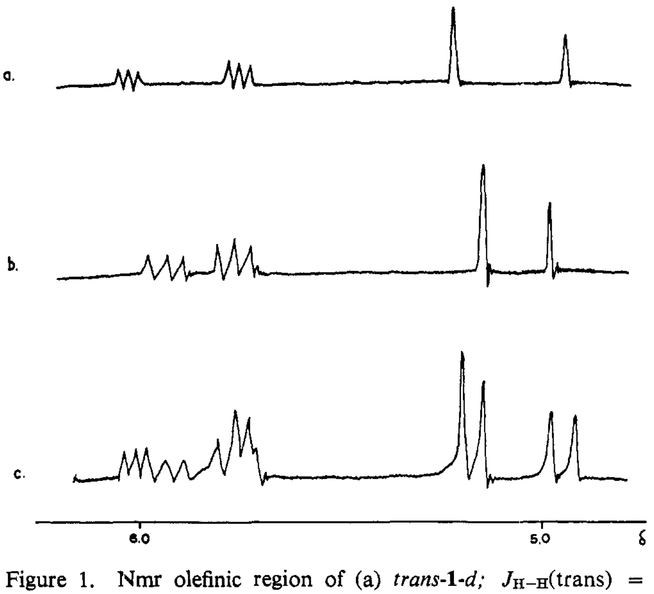
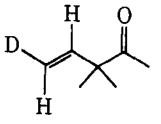
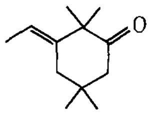


Figure 1. Nmr olefinic region of (a) *trans*-**1**-*d*; J_{H-H}(trans) = 17.3 Hz, J_{H-D}(cis) = 1.5 Hz; (b) *cis*-**1**-*d*; J_{H-H}(cis) = 10.5 Hz, J_{H-D}(trans) = 2.6 Hz; (c) irradiated *trans*-**1**-*d* isolated from acetone solution.

If twisting about the double bond is indeed an important mode by which triplet β,γ-unsaturated ketones dissipate energy, an acyclic derivative ought to cis–trans isomerize. Since this process would be hidden in **1**, the stereospecifically deuterated analog **1**-*d* was prepared. A 0.03 *M* acetone solution of **1**-*d* was irradiated briefly and concentrated by distillation, and **1**-*d* reisolated by preparative vpc. Nmr analysis[18] showed that isomerization had occurred with a quantum yield of 0.12. Longer irradiation produced a stationary-state mixture of roughly equal amounts of *cis*- and *trans*-**1**-*d* (*cf.* Figure 1). The relatively low quantum yield for triplet-sensitized isomerization and ketone disappearance suggests the existence of another pathway for radiationless decay. Indeed, even rigid β,γ-unsaturated ketones do not exhibit sensitized quantum yields greater than 0.3.[19] Although cis–trans isomerization of β,γ-unsaturated ketones has been reported previously,[20] only in the case of compound **10** was triplet sensitization demonstrated.[10a] The compounds reported here differ considerably from **10** since none of them show phosphorescence or significantly quench the type II reaction of butyrophenone. Direct irradiation of **1**-*d* also leads to isomerization but the quantum yield is only 0.02. It appears that the geminal dimethyl groups enhance α cleavage at the expense of cis–trans isomerization.[20a]



1-*d*



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[9] The ease of α cleavage is very sensitive to the nature of the alkyl group. See ref 5.

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Paul S. Engel,* Mary A. Schexnayder
Department of Chemistry, Rice University
Houston, Texas 77001

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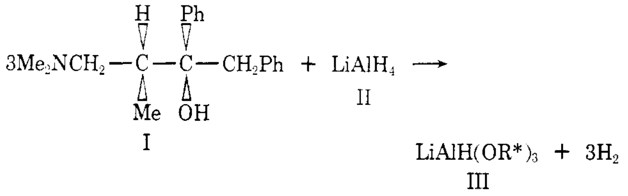
A Reversal in Stereoselectivity Depending upon the Age of a Chiral Lithium Alkoxyaluminohydride Reducing Agent[1]

Sir:

We have observed a remarkable time-dependent reversal in stereochemistry during the asymmetric reduction of methyl phenyl ketone with the chiral reducing agent formed by adding an ether solution of 2–3 equiv of (+)-(2*S*,3*R*)-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol[2] (I, R* = OH) to approximately 1 mol of lithium aluminum hydride ($LiAlH_4$, II). This reagent is symbolized by $LiAl(OR^*)_2H_2$ or $LiAlH(OR^*)_3$, where R*O represents the chiral alkoxy group from I.[3]

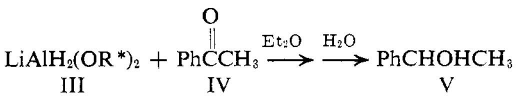


$$3Me_2NCH_2-\underset{Me}{\overset{H}{C}}-\underset{OH}{\overset{Ph}{C}}-CH_2Ph + \underset{II}{LiAlH_4} \longrightarrow \underset{III}{LiAlH(OR^*)_3} + 3H_2$$

I

Červinka and coworkers[4] have studied a series of reagents made by treating lithium aluminum hydride with various alkaloids, while Landor and coworkers[5] have studied chiral reductions using reagents prepared from lithium aluminum hydride and various sugar derivatives. Asymmetric reductions using these reagents have been reviewed.[6] In these previous studies no mention was made of dependence of stereoselectivity upon the age of the chiral reagent such as we have observed and report in this communication.

Treatment of methyl phenyl ketone (IV) with reagent III[3] (prepared by mixing 1 molar equiv of lithium aluminum hydride with 2.3 molar equiv of I) within 3 min after its preparation at 20, 3, and −65° gave (*R*)-(+)-methylphenylcarbinol (V) which was 57, 68, and 75% enantiomerically pure, respectively. However, when this chiral reagent was allowed to stand for 10 min or more, the reaction gave the *S*-(−) enantiomer of V up to a 66% excess, after 1 hr. Thus, either the *R*-(+) or *S*-(−) isomer of V can be obtained by asymmetric reduction in reasonable enantiomeric excess by using the same reagent but varying the age of that reagent between 3 min and 1 hr or more. This same stereochemical reversal was observed when the $LiAlH_4$:I molar ratio was either 1:2 or 1:3. Upon mixing $LiAlH_4$ and I in molar ratios from 1:2 to 1:3 by adding the aminocarbinol I in ether solution to a reasonably concentrated solution of $LiAlH_4$ in ether, the theoretical amount of hydrogen is evolved and a thick precipitate forms. This precipitate goes into solution on standing, on refluxing, or upon addition of a ketone substrate. However, the reversal in stereoselectivity is not associated solely with the nonhomogeneous *vs.* homogeneous nature of the reaction mixture, since a reduction conducted in a large excess of ether immediately after preparing the reagent was homogeneous and gave the *R*-(+) isomer but with reduced stereoselectivity, 29% enantiomeric excess (29% ee).



$$\underset{III}{LiAlH_2(OR^*)_2} + \underset{IV}{Ph\overset{O}{\overset{\|}{C}}CH_3} \xrightarrow{Et_2O} \xrightarrow{H_2O} \underset{V}{PhCHOHCH_3}$$

In a typical experiment a solution containing 1.02 g (3.6 mmol) of I, $[\alpha]^{27}D$ +7.96° (*c* 11.05, EtOH),[2] in 2.0 ml of ether at 0° was added to 3.0 ml of a filtered ethereal solution of lithium aluminum hydride (1.56 mmol) under nitrogen. A thick white precipitate was formed along with an immediate evolution of 3.4 mmol of hydrogen. The flask containing I was rinsed with 1.0 ml of ether and added to the mixture. Three minutes after initial mixing, 120 mg of methyl phenyl ketone (IV) in 1.0 ml of ether was added to the reagent; the precipitate disappeared almost immediately. (*R*)-(+)-Methylphenylcarbinol, 100 mg, 82% yield, $[\alpha]^{20}D$ +29.3° (*c* 8.15, cyclopentane), and the chiral inducing alcohol I, $[\alpha]^{25}D$ +7.93° (*c* 1.6, EtOH), 0.95 g, 94% recovery, were obtained after hydrolysis and work-up of the reaction mixture. Since the maximum rotation of pure V is $[\alpha]^{20}D$ +43.1° (*c* 7.19, cyclopentane), this represents 68% excess of the *R*-(+) enantiomer (68% ee). The same reaction except at −65° gave 75% ee and at room temperature 57% ee. When this reagent was made exactly as above but stirred for various lengths of time before the ketone was added, the stereoselectivity changed as follows: 4 min, 20% ee *R*-(+); 8 min, 15% ee *S*-(−) (the precipitate just dissolves after swirling for 8 min; 40 min, 62% ee *S*-(−); reflux 10 min and stirred overnight, 66% ee.

Superficially this phenomenon resembles that reported by Mislow and coworkers[7] in the asymmetric hydroboration of *cis*-3-hexene using the chiral reagent "di-3-pinanylborane"; use of freshly prepared reagent followed by oxidation gave (*R*)-(−)-3-hexanol, 20.6% ee, while use of the same reagent which had been warmed and allowed to stand 21 hr gave the (*S*)-(+)-3-hexanol, 10.7% ee. A similar finding was reported for the hydroboration of benzonorbornadiene.

The fundamental reason behind the time-dependent stereochemical reversals in these asymmetric hydroborations and our present examples of asymmetric reduction may be related or entirely different. In any event, these results point out the care required in defining reaction conditions in such stereochemical studies and

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(1) We gratefully acknowledge support of these studies by the National Science Foundation, Grant No. NSF GP-27448.

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