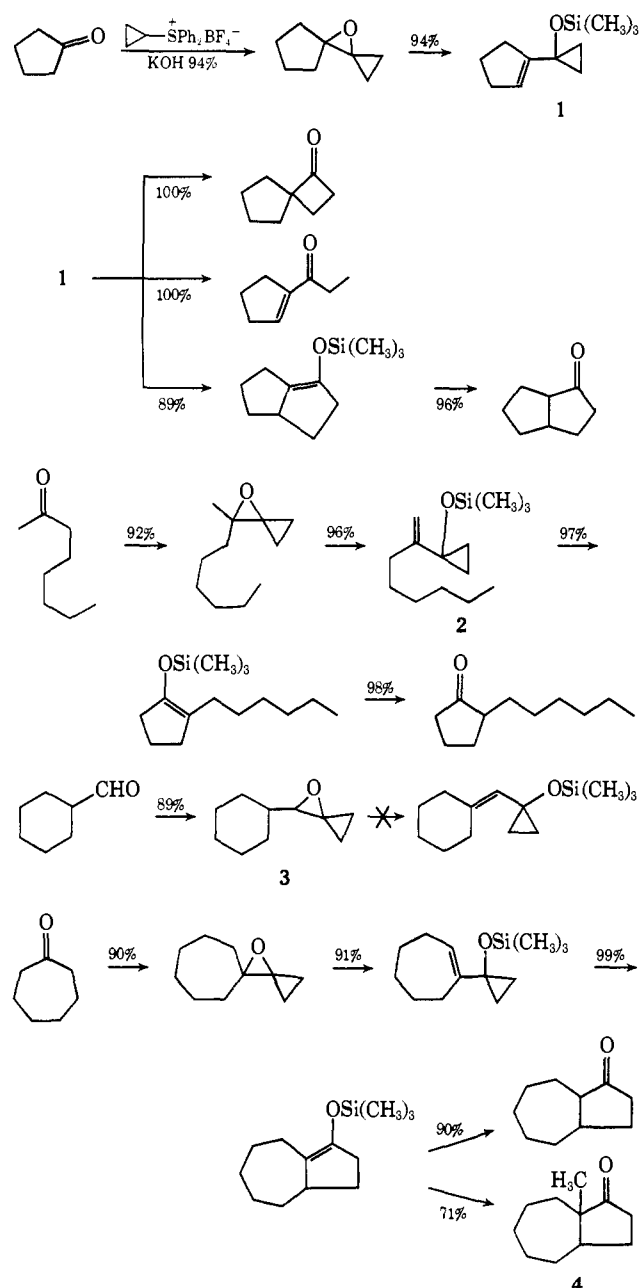


Scheme I. Cyclopentane Annellation^a

^a All yields represent isolated yields.

reaction with trimethylchlorosilane and 1–2 equiv of 1,2-dimethoxyethane followed by filtration (to remove precipitated salts), evaporation of solvent, and distillation under reduced pressure generated the silyl ether derivative **1** directly.⁶ Purification could also be achieved by chromatography on silica gel. Further characterization was provided by its reactions with acid and base. Thus, treatment with a few drops of 6 *N* aqueous hydrochloric acid in tetrahydrofuran led to rearrangement to the previously characterized spirocyclobutanone and treatment with 1 drop of a 9 *N* aqueous sodium hydroxide solution in methanol led to 1-propionylcyclopentene.⁶

Passage of a hexane solution through a conditioned⁹

(9) The hot column was washed with saturated aqueous sodium bicarbonate solution, followed by water, acetone, and hexane in that order. Further surface inactivation was achieved by either passing *O,N*-bistrimethylsilylacetamide or trimethylchlorosilane followed by diethylamine through the hot column.

hot tube packed with glass helices at 330° with a contact time of 4 sec led to smooth quantitative rearrangement to the enol silyl ethers. The much milder conditions required for the vinylcyclopropane rearrangement may be associated with stabilization of the transition state by the siloxy group. Hydrolysis unmasked the carbonyl group to give bicyclo[3.3.0]octan-2-one.^{6,10}

To examine the orientational selectivity with an unsymmetrical ketone, the case of 2-octanone was explored. Utilizing the sequence outlined above produced a single vinylcyclopropanol silyl ether identified as **2**⁶ and rearrangement generated exclusively 1-trimethylsilyloxy-2-*n*-hexylcyclopentene.⁶ Attempts to extend the reaction to include oxaspiropentane ring opening to a tertiary center, *i.e.*, **3**, failed. Thus, in agreement with Rickborn's results for the epoxide ring opening methyl reacts in preference to methylene and methine is inert.⁷

Utilizing the method of Stork¹¹ and House,¹² the initial products of rearrangement may be alkylated. Thus, treatment of the pyrolysate from the cycloheptanone case with methyl lithium in 1,2-dimethoxyethane followed by methyl iodide produced the perhydroazulenone derivative **4** with the methyl group only at the bridgehead carbon as an approximately equimolar mixture of *trans* and *cis* isomers.⁶ The assignment of configuration was based on the downfield shift of the methyl group observed for the *cis* isomer (δ 1.17) compared to that of the *trans* isomer (δ 1.13).¹³

It should be emphasized that the overall yield from starting carbonyl compound to annelated cyclopentanone is excellent, 73–83%. Combined with its regio-specificity and the ability to introduce further alkyl groups regiospecifically, this method is one of the most versatile cyclopentanone syntheses available.

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

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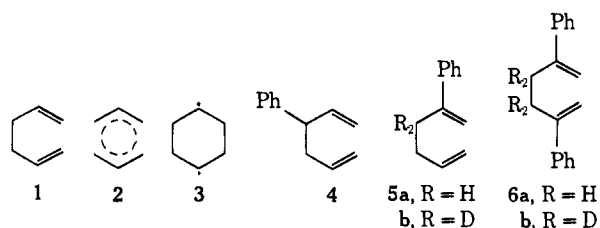
The Possible Role of 1,4-Cyclohexylene Intermediates in Cope Rearrangements

Sir:

It has been generally assumed that the Cope rearrangement is a typical pericyclic process, that of 1,5-hexadiene (**1**), for example, involving the cyclic transition state **2**. Recently, however, Doering, *et al.*,¹ have drawn attention to the possibility of an alternate two-step mechanism, formation of the new C–C bond preceding rupture of the old one so that the reaction involves a biradical intermediate. In the case of **1**,

(1) W. von E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, **27**, 5299 (1971).

this would be 1,4-cyclohexylene (3). They estimate the difference in heat of formation between 1 and 3 to be 35 kcal/mol, barely more than the observed activation energy (34 kcal/mol¹) for rearrangement of 1.



The mechanisms of reactions involving alternant hydrocarbons can often be elucidated by comparing the observed rates with those predicted by MO theory.² Indeed, for this purpose, calculations based on simple perturbational procedures³ often suffice. In the present communication it is easily seen that $\pm E$ substituents³ (e.g., phenyl) in the 3 position of 1 should have little effect on the rate of rearrangement if this takes place *via* 3 but should accelerate it if it takes place *via* 2. In the latter case, comparison of the effects of different $\pm E$ substituents in the 2 or 5 positions of 1 should show a cumulative accelerating effect if the reaction takes place *via* 3 but little or no effect if it takes place *via* 2.

We have been engaged in a detailed study of the Cope rearrangement using this approach. While the work is not yet complete, we are reporting some preliminary results which have an immediate bearing on the possible intermediacy of the biradical 3.

These results refer to the rearrangements of the 3-phenyl (4), 2-phenyl (5), and 2,5-diphenyl (6) derivatives of 1. The rearrangement of 4 was studied in the gas phase using glc; the product contained both *cis*- and *trans*-1-phenyl-1,5-hexadiene. The rearrangements of 4, 5, and 6 were followed by an nmr procedure, using the deuterated derivatives 5b and 6b with *o*-dichlorobenzene as the solvent. Comparison of these rates with the gas-phase value reported for 1 by Doering, *et al.*,¹ led to the results shown below

| Compd | Rel rate of rearrangement at 189.8 \pm 0.1 $^\circ$ |
|-------|----------------------------------------------------------|
| 1 | 1 |
| 4 | 18 |
| 5b | 41 |
| 6b | 2000 |

It will be seen that 5b rearranges much faster than 1 and indeed faster than 4. The rate of rearrangement of 6b is greater again and the ratio of rates for 6b and 5b (49) is close to that for 5b and 1 (41). There can therefore be little doubt that the rearrangements of 5 and 6 are not pericyclic reactions but involve derivatives of 1,4-cyclohexylene (3) as intermediates.

If the biradicals were transition states, the difference in activation energy between 1 and 5, or between 5 and 6, should be equal to the difference in stabilization energy between the benzyl radical and styrene (8

kcal/mol⁴). The rate differences in the table correspond to much smaller differences than this. The biradical must therefore be a stable intermediate, not the transition state.

While 5 and 6 thus seem to rearrange by the biradical mechanism, the rearrangement of 4 cannot take place in this way since it is also much faster than that of 1. Moreover, the rearrangement of 3,4-diphenyl-1,5-hexadiene is faster again.⁸ These reactions most probably do occur by the conventional pericyclic path *via* cyclic transition states analogous to 2. It therefore seems likely that 1 itself may be more or less poised between the biradical and pericyclic mechanisms and that the balance can be displaced either way by appropriate substitution.

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(4) The difference in CH bond dissociation energy between ethane and toluene is *ca.* 13 kcal/mol.⁵ If the Ph-C bond in toluene were localized,⁶ the CH bond energy in toluene would be reduced by *ca.* 5 kcal/mol, due to the conversion of a sp^3-sp^2 C-C bond in toluene to a sp^2-sp^2 C-C bond in the benzyl radical.⁷ The extra stabilization (8 kcal/mol) of the benzyl radical must then be ascribed to resonance stabilization.⁶ In the conversion of styrene to benzyl radical the Ph-C bond remains of unchanged type (sp^2-sp^2). The exocyclic bonds in styrene are moreover localized.⁶ Consequently the conversion of styrene to benzyl radical should be resonance assisted to the extent of 8 kcal/mol.

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Photoelectron Spectra of Cyclic Ethers

Sir:

For over 30 years there has been widespread interest in the interactions of nonadjacent groups.¹ In the past, electronic absorption spectroscopy was very useful in determining if such interactions existed. However, ground-state and excited-state interactions could not be distinguished by uv spectroscopy. Recently photoelectron spectroscopy (PES) has proven to be extremely useful in evaluating these interactions in the ground state, assuming the validity of Koopmans' theorem.² Heilbronner and coworkers³ have clearly demonstrated the use of PES in studying π_{CC}, π_{CC} interactions in dienes, n_N, n_N interactions in nitrogen compounds, and n_O, n_O interactions in dicarbonyl compounds. We⁴ and others⁵ have found PES useful in the study of the π_{CC} and n_O levels in unsaturated ketones. Now we would like to report our results of a

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