

Communications to the Editor

Photochemistry of Large Ring 2-Phenylcyclopanones. Formation of Cyclophanes and Encapsulation by a Ship in Bottle and by a Reptation Strategy

Xue-gong Lei, Charles E. Doubleday, Jr.,*
Matthew B. Zimmt, and Nicholas J. Turro*

Department of Chemistry, Columbia University
New York, New York 10027

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The photochemistry of five- and six-membered cyclopanones has played an important role in the development of mechanistic organic chemistry and in our knowledge of biradicals.^{1,2} The dominant primary photochemical process of these alkanones is homolytic α -cleavage (type I process) of a $T_1(n, \pi^*)$ state which produces a triplet biradical. The latter is stabilized after intersystem crossing to a singlet biradical by disproportionation reactions (to generate ketenes and/or enals) and by combination reactions (to regenerate the starting structure or an isomer). For example, the photolysis of 2-phenylcyclopentanone and 2-phenylcyclohexanone yields alkenals in good yields.^{3,4} We report that the photolysis of larger ring cyclopanones (10, 11, 12, and 15 membered) produce cyclophanes via a previously unanticipated and unprecedented combination process of biradical stabilization. We also report that the size/shape change that occurs in the photochemical cyclopanone to cyclophane conversion can be exploited as the basis of a ship in bottle and of a reptation strategy to irreversibly encapsulate organic molecules in the super cage voids of zeolites.

The cyclopanones K_n (where n labels the original ketone ring size, Scheme I) were prepared by conventional synthetic methodologies⁵ and characterized by conventional spectroscopic methods.⁶ In the case of K_9 , photolysis in a variety of solvents (pentane, methanol, DMF) results in formation of enals (*cis*-EA₉, $x = 6$, and *trans*-EA₉, $x = 6$) in good yield (Table I). No evidence for the cyclophane structure C_9 could be found by NMR or GC analysis of reaction mixtures. In contrast, photolysis of K_{10} , K_{11} , K_{12} , or K_{15} in the same solvents resulted in formation of cyclophanes C_{10} , C_{11} , C_{12} , or C_{15} , respectively, in yields given in Table I. The structure of C_{10} was definitely established by X-ray crystallographic analysis⁷ and by ¹H NMR, IR, and GC/MS analyses. The structures of C_{10} , C_{11} , C_{12} , and C_{15} were established by excellent spectral correlations with C_{10} , especially ¹H NMR analysis.⁸

The formation of C_n is postulated to result from para coupling of the biradical intermediate B_n to produce a precursor (PC_n) to the cyclophanes (Scheme I). Nelsen and Bartlett^{9a} first reported

Scheme I

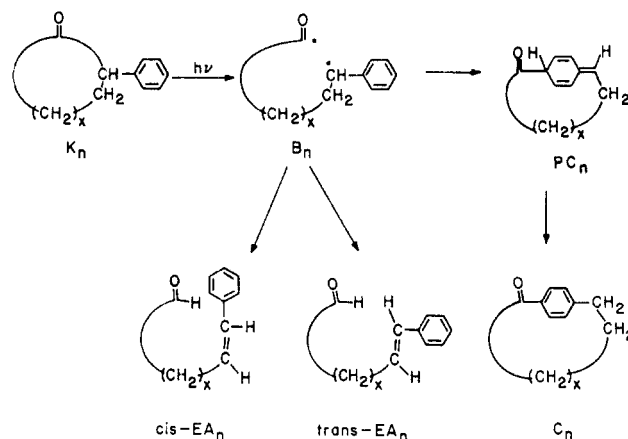


Table I. Quantum Yield and Product Distribution Yields for Photolysis of α -Phenylcyclopanones^a

ketone (K_n)	Φ_{-k}^b	hexane			CH ₃ OH		
		C_n	<i>cis</i> -EA _n	<i>trans</i> -EA _n	C_n	<i>cis</i> -EA _n	<i>trans</i> -EA _n
$n = 9$	0.3	0	0	60	0	1	54
$n = 10$	0.6	62	0	5	65	0	8
$n = 11$	0.6				94	0	5
$n = 12$	0.5	69	0.1	1	89	1	9
$n = 15$	0.2	61			68		

^aYields were measured at <15% conversion. Ethanol/octadecane was added as an internal standard to the irradiated samples which were treated overnight before analysis. This procedure allowed reproducible conversion of PC_n (Scheme I) to C_n by VPC analysis. Yields are based on starting ketone disappearance. ^bQuantum yields were determined in methanol and are relative to α -phenylcyclohexanone ($\Phi = 0.6$, benzene) as per ref 3.

para coupling in the dimerization of cumyl radicals and McBride^{9b} characterized the system thoroughly. From CIDNP evidence, Fischer^{9c} proposed para coupling of the $C_6H_5CH_2\dot{C}O\dot{C}H_2C_6H_5$ radical pair produced by photolysis of dibenzyl ketone (DBK) to produce a semibenzyl product,¹⁰ which then either cleaved back to the radical pair or was stabilized by a hydrogen shift to yield 1-phenyl-4-methylacetophenone (PMAP). However, the chemical yield of PMAP was too low to detect by conventional analyses. It was later discovered that PMAP was produced in varying yields by photolysis¹¹⁻¹³ in micelles,¹¹ on porous silica,¹² and on zeolites,¹³ the latter reaction environments being viewed as microscopic reactors that encouraged geminate pair reactions and para coupling. With these results in mind, we envisioned a ship in bottle and a reptation strategy that could exploit the size/shape change that occurs in the overall $K_n \rightarrow C_n$ transformation to irreversibly encapsulate C_n in an intracrystalline super cage of a zeolite. Molecular models suggest that NaX, a faujasite zeolite possessing an 8-Å pore opening to its 13-Å internal super cages,¹⁴ would allow facile entry of K_n into the zeolite internal surface but that C_n (which possesses a larger size than K_n), once inside a super cage, would not be able to escape. If the process $K_n \rightarrow B_n \rightarrow C_n$ could

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(5) The following synthetic sequence was followed for preparation of α -phenyl ketones, K_n : the parent cyclopanone was treated with (a) PhLi, (b) TsOH, (c) B₂H₆, (d) H₂O₂, HO⁻, and (e) pyridinium chlorochromate.

(6) The NMR, IR, UV, and MS spectra were fully consistent with the assigned structures. Details will be published in the full paper.

(7) Complete data on the X-ray parameters will be published in the full paper.

(8) The AA'XX' four-proton pattern of the phenyl region of the cyclophanes is strikingly characteristic of these structures.

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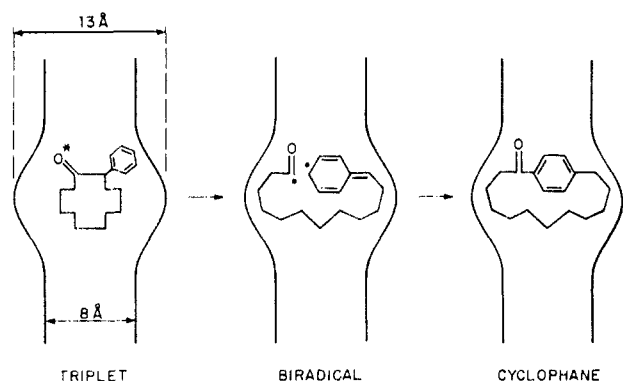


Figure 1. Ship in bottle strategy for encapsulation in a zeolite supercage. The cyclanone K_{12} is cleaved photochemically to the biradical B_{12} and then cyclizes to the cyclophane C_{12} . All of these processes occur within the NaX zeolite supercage. The size/shape of C_{12} prevents its escape from the supercage.

be made to occur entirely within a super cage, the ship in bottle strategy could achieve irreversible encapsulation of C_n in the internal surface of the zeolite.

To test for the experimental realization of this strategy, K_{12} was adsorbed into the internal super cages of NaX zeolite by conventional deposition from pentane solvent.¹⁵ Before photolysis, K_{12} could be reversibly extracted from the zeolite. Photolysis reduced the yield of extractable K_{12} , and C_{12} was not observed in the extracts. However, it was found that C_{12} is produced by photolysis of K_{12} adsorbed on NaX, since dissolution of the entire zeolite framework with HCl followed by neutralization with NaOH and ether extraction resulted in a good yield (ca. 80%) of C_{12} . Since C_{12} is not adsorbed into NaX under our reaction conditions, but K_{12} is, the ship in bottle strategy proved successful (Figure 1); i.e., a reactant (K_{12}) whose size and shape allow passage through the pores leading to the NaX super cage is converted photochemically into a product whose size and shape prevent exit from the super cage. Similar results were observed for K_{10} , K_{11} , and K_{15} .

From molecular models a variation of the ship in bottle strategy is apparent for the K_{15}/C_{15} system. This strategy, termed reptation, involves formation of a biradical from photolysis of a cyclanone that is too large to enter the zeolite framework. The biradical, although formed on the external surface, can enter the internal surface by a slithering motion, or reptation, through the pore leading to a super cage. Once inside a super cage, cyclization to a cyclophane causes encapsulation within the super cage. Empirically, it was found that neither the ketone, K_{15} , nor the cyclophane, C_{15} , is adsorbed through the pores of CaX, the Ca^{2+} exchanged form of NaX. However, it is expected that B_{15} , produced by photolysis, can reptate through the zeolite pore and enter the super cage. The process $K_{15}(\text{out}) \rightarrow B_{15}(\text{out}) \rightarrow B_{15}(\text{in}) \rightarrow C_{15}(\text{in})$ would encapsulate the cyclophane internally. This expectation was realized experimentally. After deposition from pentane and drying, >90% of the adsorbed K_{15} and C_{15} were rapidly extracted from CaX with chloroform,¹⁵ indicating little adsorption of either molecule on the internal surface. Upon photolysis of adsorbed K_{15} , however, C_{15} is formed and encapsulated internally as evidenced by the failure of normal extraction

(15) NaX molecular sieves were obtained from Union Carbide (Type 13x powder, lot no. 945083020004-S-1) and heated at 500 °C for 1 h immediately before use. The ketones were adsorbed onto the zeolites from pentane solutions (ca. 1% ketone wt/wt). The pentane was removed by evaporation followed by 12 h at 10^{-3} torr. The samples were maintained under vacuum and tumbled during photolysis (313 nm) at ambient temperature. When K_n or C_n is deposited on NaX zeolite followed by extraction with $CHCl_3$, the amount recovered depends strongly on the time (0.5–12 h) under vacuum during drying after deposition and on the soaking time (0.5–12 h) during the $CHCl_3$ extraction. Shorter drying time or longer soaking time yields a higher percent recovery. However, when K_n or C_n is deposited on 4A zeolite (4-Å openings), all or nearly all the material is recovered after $CHCl_3$ extraction and the percent recovery is independent of the drying or soaking time. Since no adsorption inside the zeolite is possible with 4A, the difference is presumably due to adsorption inside the NaX super cage structure.

to remove C_{15} from the zeolite and the requirement to dissolve the entire zeolite framework in order to release and extract the cyclophane (80% yield).

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Stereospecific Synthesis of Alkenyl Fluorides (with Retention) via Organometallic Intermediates

Seung Han Lee and Jeffrey Schwartz*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

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Fluoroorganics are of demonstrated importance in organic chemistry because of their use as medicinals, as tools in medical diagnosis, and in fundamental studies of biochemical and metabolic processes.¹ Consequently, the development of methodology for the specific introduction of fluorine into a variety of types of organic substrates remains a field of active endeavor. Unfortunately, many of the procedures that have been developed for this purpose employ highly reactive and often corrosive materials such as F_2 ,² XeF_2 ,³ $FCIO_3$,⁴ CF_3OF ,⁵ CH_3COOF ,⁶ or fluoroamine derivatives.⁷ As well, although many routes are available for the creation of fluoroalkanes, synthetic methodology for the synthesis of fluoroalkenes has not been as well studied;⁸ in particular, methods for the stereospecific preparation of alkenyl fluorides have not been realized heretofore.⁸ Cleavage reactions of alkenylmetallics such as alkenylmercurials,⁹ alkenylaluminums,¹⁰ alkenylboranes,¹¹ or alkenylzirconiums¹² using "positive" halogen reagents have been shown to be of use for the preparation of alkenyl chlorides, bromides, or iodides. However, analogous

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