PNP and αCD·PNP complex through the cellulose membrane discussed above. The observed differences in the diffusional rate constants is in accord with that expected from differences in the hydrodynamic radii. The apparent "spherical" radii, estimated from CPK molecular models, for PNP and αCD·PNP are 2.2 ± 0.8 and 6.6 ± 0.5 Å, respectively. The ratio of these radii, 3.0 ± 0.9, is not significantly different from 3.6, the value of the inverse ratio of the observed diffusional rate constants for these species.[11] The greater mobility of αCD relative to the αCD·PNP complex also seems reasonable in view of the solvent access to the interior cavity of the free species.

Studies are in progress to further characterize and extend this oscillatory kinetic phenomena, as a model for active transport in biological membranes.

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(7) An aqueous solution containing 9 mM PNP and a variable amount of αCD was equilibrated against deionized water. Equilibrations were followed by the increase in either conductance or optical absorption at 390 nm.
(8) Good first-order kinetics were observed through >90% of each equilibration reaction. Measurements were made in an apparatus consisting of two chambers separated by a 13.75 cm^2 (2.5 × 5.5 cm) section of membrane, thermostated at 28.0 °C. Control experiments in which the membrane surface area was varied over a factor of four revealed no significant effect on the observed rate constants.
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Evidence for a Radical-Anion Pathway of a Phenylcyclopropyl Ring Cleavage in the Presence of Potassium *tert*-Butoxide

Sir:

2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**1**) has been reported to undergo ring opening when treated with potassium *tert*-butoxide (KO-*t*-Bu) in dimethyl sulfoxide to give after workup 2,3,4-triphenylbicyclo[3.2.1]oct-2-ene (**2**).[1,2] This reaction was presumed to proceed via a forbidden disrotatory ring opening of the cyclopropyl anion formed by deprotonation and is the only example of such a reaction which proceeds facilely. Although **1** is probably more strained than a simple cyclopropane,[4] the known high-energy, symmetry-imposed barrier for disrotatory cyclopropyl anion openings[5] and the short lifetime expected for the cyclopropyl anion in Me_2SO[6] cast doubt on the validity of the proposed mechanism and suggested that further study of the reactions of **1** with strong bases should prove interesting. We report herein the results of our studies from which we infer that conversion of **1** to **2** occurs by a process involving reduction of **1**, radical-anion cyclopropyl bond cleavage, rearrangement, and oxidation of an intermediate to give **2**. Our interpretation requires that KO-*t*-Bu/Me_2SO and related base solutions can act as electron donors and suggests that other reactions related to the conversion of **1** to **2** may proceed by radical-ion pathways which were not previously considered.

Treatment of **1** with KO-*t*-Bu/Me_2SO at 70 °C as described by Mulvaney[1] or at 25 °C for 20 h gave **2**. Similarly **1** was converted to **2** by treatment with KO-*t*-Bu/hexamethylphosphoramide (HMPA) at 25 °C for 24 h or by dimsylpotassium (from KH and Me_2SO) in Me_2SO at 70 °C for 24 h. However, treatment of **1** with several other strong bases failed to produce **2**.[8] When **1** was treated with *n*-butyllithium–tetramethylethylenediamine complex in hexane at 25 °C, a purple solution (λ_{max} shoulder at 510–520 nm) was formed. Addition of deuterium oxide to this solution gave **1** which contained from zero to four deuterium atoms by mass spectrometry.[10] It is most likely that **3** was formed in this reaction since 1-lithio-1,2-diphenylcyclopropane (**4**) has λ_{max} at 490 nm.[11] Polydeuterated **1** could be formed by initial deuteration on an ortho or para position of the phenyl ring at C-3 to give, for example, **5** which should exchange protons readily.[12] The ^1H-decoupled ^{13}C NMR spectrum of polydeuterated **1** showed, among other minor changes, a greatly diminished intensity for the signal assigned to the para carbon atom of the phenyl ring on C-3 of **1** which is consistent with loss of Overhauser enhancement due to significant deuterium substitution.[13] Since **3** is stable, a cyclopropyl anion cannot be an intermediate in the pathway for conversion of **1** to **2**.

We conclude that **1** is converted to **2** by the mechanism shown in Scheme I. Electron transfer, presumably initially from base, to **1** gives radical anion **6** which cleaves to **7**. Subsequent rearrangement of **7** gives **8** which resembles a stilbene radical anion. Transfer of an electron from **8**, possibly to another molecule of **1**, produces **2**. In addition to the evidence

Scheme I

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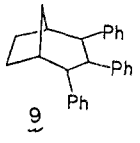
already given above, the following facts support this mechanism. Cyclopropyl rings containing phenyl groups are readily cleaved by alkali metals and sodium naphthalenide (NaNp) to give reduced products;[14] similarly, **1**, when treated with NaNp in THF, gives a mixture of isomers of general structure **9**.[15] Good oxidizing agents such as nitrobenzene are known to be reduced to radical anions in KO-*t*-Bu/Me_2SO solutions,[16a] and *p*-dinitrobenzene is reduced by direct electron transfer from OH^- in aqueous Me_2SO.[16b] We believe that such reductions[16] show that electron transfer from KO-*t*-Bu or dimsyl anion to **1** can occur. Stilbene radical anions are known to donate electrons to neutrals or accept a second electron depending on reaction conditions,[17] which is similar to the behavior seen for **8** where further reduction (NaNp in THF) or oxidation (KO-*t*-Bu/Me_2SO) occur. We do not know by what process **7** is converted to **8** since 1,2 shifts of protons or hydrogen atoms are not generally observed, but speculate that an intramolecular rearrangement could be occurring.



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We were not able to observe an ESR spectrum from a reacting mixture of **1** and KO-*t*-Bu in Me_2SO, but a reaction half-life of 1 h would require that radical intermediates have an average lifetime of greater than 1×10^{-3} s to obtain a steady-state concentration of 1×10^{-9} M. Thus these reactions which appear to proceed over several hours may never have detectable concentrations of intermediates if all steps after the first are fast.

Finally, we believe that the mechanism shown in Scheme I is supported by the fact that other reactions can be explained by related pathways. Miller[14b] observed that the major product formed by treatment of dibenzonorcaradiene with lithium metal was not a reduction product but 9-methyl-phenanthrene, and Shatenshtein[18] has reported that *trans*-1,2-diphenylcyclopropane forms 1,3-diphenylpropene upon treatment with KO-*t*-Bu in Me_2SO or HMPA.[19] In both cases mechanisms similar to that in Scheme I would explain formation of these products. Further, the "carbon Claisen" reactions of *trans*-1-phenyl-2-vinylcyclopropane reported by Marvel[20a] and of 1-phenylbutenes reported by Doering[20b] occur in the presence of KO-*t*-Bu. The authors[20] rationalized that the base isomerizes, and thus traps, the initial "carbon Claisen" product, but based on our results an alternative radical-anion pathway for these reactions must now be considered.[21,23]

In summary, we have shown that cleavage of the cyclopropane ring in **1** does not occur via a disrotatory cyclopropyl anion opening. The reaction of **1** with KO-*t*-Bu in Me_2SO or HMPA or with dimsylpotassium in Me_2SO appears to proceed by a radical-anion pathway. In addition, the potential for electron-transfer pathways occurring in reactions of other aryl compounds with these bases has been presented.

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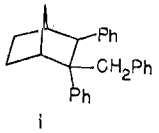

i

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