electron-exchange luminescence,[15,16] it was especially important to determine its triplet acetone yield by a chemical titration technique. Even if this complication were not applicable, the observed low triplet yield[8] would require correction for triplet states derived via intersystem crossing from singlet excited acetone.

With the benzonorbornadiene (**2a**) titrant, it was not possible via a double reciprocal plot to determine the triplet acetone yield from **1a**. The scatter of data points was too great to afford reliable intercepts. Consequently, at the highest, feasible [**1b**] of 0.04 M in toluene and [**2a**] of 0.04 M, the [**2b**]/[**2a**] ratio was determined relative to **1a** under identical conditions. Using a triplet acetone yield of 31% determined for **1a**, ten independent triplicate determinations gave a value of 1.1 ± 0.1% (Table I) of triplet acetone from **1b**. Our results check well with the recent determination via direct acetone phosphorence emission.[12] Furthermore, they establish the lower quantitative detection limit of triplet excitation by means of **2a** since the tricyclic photoisomer **2b** was just barely visible in the VPC trace.

The dioxetane **1c** was utilized to establish the upper temperature limit for our chemical titration method, since **1c** is to date still the most stable dioxetane.[5] Heating of benzene solutions 0.1 M in **1c** and variable concentrations (0.209 to 0.523 M) in **2a** in sealed tubes at 145 °C for 24 h secured complete decomposition. Determination of the [**2b**]/[**2a**] ratios by GLC as described for **1a**[14] and construction of a double reciprocal plot of the chemical yield of **2b** vs. **2a** gave intercept values of 125 ± 7. From this data and an isomerization efficiency of 50% for **2a** to **2b**,[10] we calculate a triplet adamantanone value of 1.6 ± 0.1% (Table I). Control experiments confirm that, under the thermolysis and GLC conditions, **2b** decomposes to the extent of only 3%, but it does not revert to **2a**, while **2a** is stable under these conditions. Furthermore, control experiments showed that the photoisomerization quantum yield is independent of temperature. Thus, the diadamantylidene-1,2-dioxetane **1c** represents the upper temperature limit for chemical titration of thermally generated triplets with benzonorbornadiene.

The determination of the triplet ester yield from the dioxenedioxetane **1d** was undertaken to illustrate the diversity of the method. Originally the di-π-methane rearrangement of **2a** into **2b** was shown[10] to be effective for ketones with triplet energies higher than 68 kcal/mol. Since the triplet energy of the diester derived from **1d** is expected to be ~79 kcal/mol,[17] **2a** should be applicable for the titration of the triplet ester derived from **1d**. Decomposition of benzene solutions 0.1 M in **1d** and at variable concentrations (0.209 to 0.523 M) in **2a** in sealed tube at 80 °C for 3 h gave an intercept value of 9.0 ± 0.2 from the double reciprocal plot of the chemical yield of **2b** vs. [**2a**]. This afforded a triplet diester yield of 22 ± 1% (Table I). Thus, this chemical titration method is not restricted to ketone triplet states. More importantly, dioxenedioxetanes are CIEEL active,[13] and the present chemical titration technique might be the only reliable method for the quantitation of such triplets.

In summary, the di-π-methane isomerization of **2a** to **2b** constitutes a convenient, reliable, and general method for the chemical titration of thermally generated triplet states. The method is sensitive, detecting triplet yields as low as 1%, can be used at elevated temperature up to 145 °C, and applies to a variety of carbonyl triplets such as ketones and esters as long as the triplet energies are 68 kcal/mol or greater.

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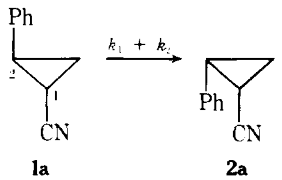
Secondary Deuterium Kinetic Isotope Effects in the Thermal Stereomutations of 1-Cyano-2-phenylcyclopropanes

Sir:

A recent kinetic study demonstrated that interconversion of *cis-* and *trans-*1-cyano-2-phenylcyclopropane occurs through one-center epimerizations at C(1) and C(2); no two-center processes contribute to the cis–trans isomerization, so that the experimentally observable rate constant for the reaction *dl*-**1a** → *dl*-**2a**, $k(\mathrm{t} \rightarrow \mathrm{c})$, is equal to the sum of two mechanistic rate constants ($k_1 + k_2$).[1,2]



1a **2a**

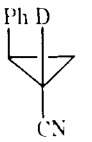
In conjunction with this study[1] we had an opportunity to measure two distinct secondary deuterium isotope effects[3] on the one-center epimerizations, starting with compounds **1b–d** or the corresponding cis isomers **2b–d**.

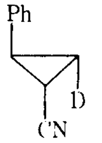
The deuterated systems **1b–d** and **2b–d** were available from or were synthesized by methods analogous to those employed in our earlier work.[1] The thermal equilibrations starting with

Table I. Rate Constants for Thermal Trans to Cis Isomerizations of Deuterium-Labeled 1-Cyano-2-phenylcyclopropanes

reaction	T, °C	$(k_1 + k_2)$, 10^{-5} s^{-1}	C(1)(k^H/k^D)	C(1)(k^H/k^D)C(3)(k^H/k^D)	C(3)(k^H/k^D)
1a → **2a**	242.1	1.30 ± 0.02			
1b → **2b**	242.1	1.22 ± 0.01	1.07 ± 0.02		
1d → **2d**	242.1	1.09 ± 0.04[a,b]		1.19 ± 0.05	1.13 ± 0.05[c]
1a → **2a**	246	1.58 ± 0.04			
1c → **2c**	246	1.40 ± 0.03			1.13 ± 0.04

[a] $k_1 = 0.76 \pm 10^{-5}$ s^{-1}; $k_2 = 0.33 \times 10^{-5}$ s^{-1}. [b] Observed; 90% d_1 at C(1). [c] Corrected for incomplete labeling at C(1).


1b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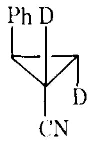
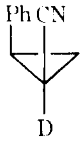
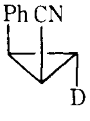
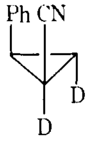

1d


2b


2c


2d

1i or **2i** in 1-methylnaphthalene solutions were followed by GLC on a Carbowax 20M column, with 8 to 12 kinetic points per system. Deuterated and unlabeled samples were pyrolyzed simultaneously in the kinetic bath in sealed ampules. The concentration vs. time data gave rise to the rate constants and isotope effects summarized in Table I.

Substitution of deuterium for hydrogen at C(1) leads to a normal secondary isotope effect, $(k_1 + k_2)^H/(k_1 + k_2)^D$ $^{C(1)}$ = 1.07 ± 0.02; if the entire change in rate constant with deuterium substitution is due to k_1, and k_1 for **1b** → **2b** is ~70% of $(k_1 + k_2)$ as it is for the reaction **1d** → **2d**, then k_1^H/k_1^D $^{C(1)}$ = 1.09 ± 0.02. The magnitude of the isotope effect associated with deuterium substitution at C(3) is larger; the two independent determinations of $(k_1 + k_2)^H/(k_1 + k_2)^D$ $^{C(3)}$ in Table I average to 1.13 ± 0.02. This large β secondary deuterium isotope effect points to a high degree of interaction between C(1) and C(2) with the H-C(3) bonds in the transition state.[4]

Crawford and Mishra[5] and Al-Sader and Crawford[6] have observed β deuterium isotope effects of 1.06 ± 0.03 for pyrolytic decomposition of 4-methyl-1-pyrazoline and the 4-deuterio derivative, and for 1-pyrazoline and 4-deuterio-1-pyrazoline, at temperatures between 225 and 245 °C, and have noted that the effects may be due to hyperconjugative interactions in a *O,O*-trimethylene or π-cyclopropane species.

It may be that a π-cyclopropane serves as an entity through which the k_1, k_2, and k_{12} epimerizations of cyclopropanes such as **1** occur; the relative values of these rate constants would then depend on partitionings between conrotatory and disrotatory modes of ring opening and ring closing or on kinetic competition between single 180° rotations of terminal groups in the trimethylene species and ring closure.[4,7]

The kinetic isotope effect observed for D-C(3) substitution on the reaction **1** → **2** is relatively large even though the system bears substituents that one may presume are effective in delocalizing and stabilizing a *O,O*-trimethylene species; less substituted cyclopropanes might exhibit still larger β deuterium kinetic isotope effects. This possibility is relevant to a recent kinetic study of the thermal stereomutations of optically active *trans*-1,2-dideuteriocyclopropane, which recognized the likelihood of and assumed the kinetic consequences of a normal isotope effect for cleavage of a C-C bond α to a deuterium atom, but which did not consider β secondary deuterium isotope effects.[8] If there is a substantial β isotope effect on k_{12} and k_{13} of 1,2-dideuteriocyclopropane, k_1 might be a larger fraction of k_{12} than has been suggested. If, for example, k_{12}/k_{13} were 1.05, then k_1 would be 19 ± 5% of k_{12}; the assumption[8] that k_{13}/k_{12} = 1.1 and the experimental rate constants[8] for racemization and cis-trans isomerization give k_1 equal to 4 ± 5% of k_{12}.

There are clear and challenging experimental tasks ahead: determination of α and β secondary deuterium isotope effects on individual k_i and k_{ij} rate constants in appropriate representative substituted cyclopropanes and in isotopically labeled cyclopropane itself.

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Reduction of Nitrate Ion by $(bpy)_2pyRu(OH_2)^{2+}$

Sir:

The oxy anions NO_3^- and ClO_4^- are strongly oxidizing[1] and yet are sufficiently unreactive under normal conditions that they are frequently used as the anion in "inert" electrolytes or as the counterion in the preparation of metal complex salts. Facile reduction of NO_3^- is a particularly interesting mechanistic problem because (1) NO_3^- is a key source of inorganic nitrogen in biological systems via the molybdenum-based enzyme nitrate reductase,[2] and (2) NO_3^- represents a source of stored chemical oxidizing energy which may be useful in the oxidation of organic compounds[1b] or possibly in fuel-cell applications.[3] In the course of our studies on aquo and related 2,2′-bipyridine complexes of ruthenium for use in redox catalysis,[4] we have observed some remarkable chemistry in which aquo complexes of ruthenium are oxidized in solution by NO_3^- or ClO_4^- at room temperature.[5] Earlier studies[6] have shown that ruthenium complexes can be especially reactive toward ClO_4^-, and our initial results on the reduction of NO_3^- by