K can be derived if six nearest magnetic neighbors are assumed. The antiferromagnetic ordering temperature will be below 1 K. These results are corroborated by specific heat studies on this compound,[13] which are found to yield a sharp $\lambda$-type anomaly at $T_c = 0.456$ K, an ordering temperature slightly higher than that of the perchlorate.

The superexchange path in $[Co(C_5H_5NO)_6](ClO_4)_2$ and $[Co(C_5H_5NO)_6](BF_4)_2$ has been assigned[4] a Co-O-O-Co interaction, with an O-O separation of 5.6 Å. It is especially important that the rings turn away, in propeller fashion, from the metal atoms. The great similarity in the properties displayed by the nitrate suggests that the same superexchange path is available here. Final discussion awaits a full crystal structure analysis, which is in progress. One is also led to suggest that O-O contact on neighboring molecules not only provides a suitable exchange path, but may also be a contributing factor to the particular crystal lattice structure assumed by these molecules.

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**Energy Acquisition, Storage, and Release.
Photochemistry of Cyclic Azoalkanes as Alternate
Entries to the Energy Surfaces Interconnecting
Norbornadiene and Quadricyclene**

*Sir:*

The photochemical rearrangement of norbornadienes to quadricyclenes is a useful reaction of wide synthetic scope.[1] We selected the cyclic azoalkanes $1^2$ and $2^3$ as potential precursors to the norbornadienyl and quadricyclenyl diradicals ($D_N$ and $D_Q$), respectively. It was anticipated that a quantitative investigation of the photochemistry of 1 and 2 would reveal significant information relevant to the mechanism of the photointerconversions of the parent systems norbornadiene (N), and quadricyclene (Q) by providing independent routes to $D_N$ and $D_Q$ and thereby assist in elucidating the nature of the energy surfaces along which N and Q may be interconverted[4] (Scheme I).

Scheme I. Reactions of 1 and 2 to form N and Q.
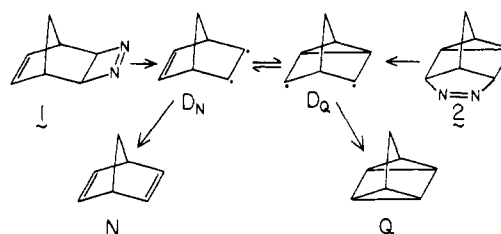


The photolysis of 1 and 2 under a variety of conditions led[2,3] to loss of $N_2$ and formation of N and Q in nearly quantitative yield and with good quantum efficiencies (Table I). In all cases care was taken to assure that N and Q were formed as primary products and not via secondary thermal or photochemical processes.

The yields of Q and N are ~90% and 10%, respectively, upon triplet sensitization of 1 or 2 as well as upon *direct* $S_0 \rightarrow T_1$ excitation[5] of 1 or 2. From these results we conclude that the triplet state of 1 or 2 upon loss of $N_2$ yields a triplet diradical which proceeds with high selectivity to Q.[6] Upon direct $S_0 \rightarrow S_1$ excitation of 1, the relative yields of N and Q are similar to those achieved by triplet sensitization; thus, we conclude that 1 undergoes efficient intersystem crossing from its $S_1$ state. In contrast, the direct $S_0 \rightarrow S_1$ excitation of 2 yields N as the *major* product, from which we conclude the intersystem crossing is *inefficient* from $S_1$ of 2.[7]

From the data in Table I, it appears that, if diradicals $D_N$ or $D_Q$ are produced in a singlet state, they proceed preferentially to yield N. In contrast, if $D_N$ or $D_Q$ are produced in a triplet state, preferential formation of Q is observed.

An exceedingly intriguing and important problem in understanding photochemical reactions concerns the geometry for which radiationless transitions occur from upper surfaces to the $S_0$ surface.[9] Diradicaloid geometries have been postulated to serve as guides to the regions on excited surfaces through which molecules may "jump" to the ground-state surface.[9] It is thus anticipated that the favored geometry for a radiationless transition to $S_0$ may be determined by the geometry of the minimum on the $S_1$ or $T_1$ surface which best serves to deliver excited molecules back to $S_0$.

Our results suggest that *the excited singlet surface connecting the N and Q structures possesses a minimum which*

**Table I.** Photochemistry of Azoalkanes 1 and 2

| Compd | Reaction conditions | $\phi$ | % N | % Q |
|---|---|---|---|---|
| 1 | $S_0 \rightarrow S_1$ (RT)[a] | $0.36^b$ | $29^c$ | $71^c$ |
| | $S_0 \rightarrow S_1$ (−78 °C) | | 9 | 91 |
| | $S_0 \rightarrow T_1$ (RT)[d] | | 10 | 90 |
| | $^3$Sens (RT) | $0.40^e$ | 10 | 90 |
| | $^3$Sens (−78 °C)[f] | | 12 | 88 |
| | Thermolysis[g] | | ~95 | ~5 |
| 2 | $S_0 \rightarrow S_1$ (RT)[a] | $0.44^b$ | $63^c$ | $37^c$ |
| | $S_0 \rightarrow S_1$ (−78 °C) | | 29 | 71 |
| | $S_0 \rightarrow T_1$ (RT)[d] | | 11 | 89 |
| | $^3$Sens (RT) | $0.57^e$ | 10 | 90 |
| | $^3$Sens (−78 °C)[f] | | 10 | 90 |
| | Thermolysis[g] | | ~100 | 0 |

[a] Pentane solvent unless noted otherwise. [b] Based on azoalkane disappearance and product formation. [c] Percentages include only N, Q products. At times small amounts of norbornene, toluene, and cycloheptatriene were observed but not included in percentages. [d] See ref 5. [e] Based on product formation. [f] The solvent was $CFCl_3$. At room temperature, the results in $CFCl_3$ were the same as in pentane. [g] Thermolysis temperature 90-110 °C. Quadricyclene was shown to be stable under the reaction conditions.
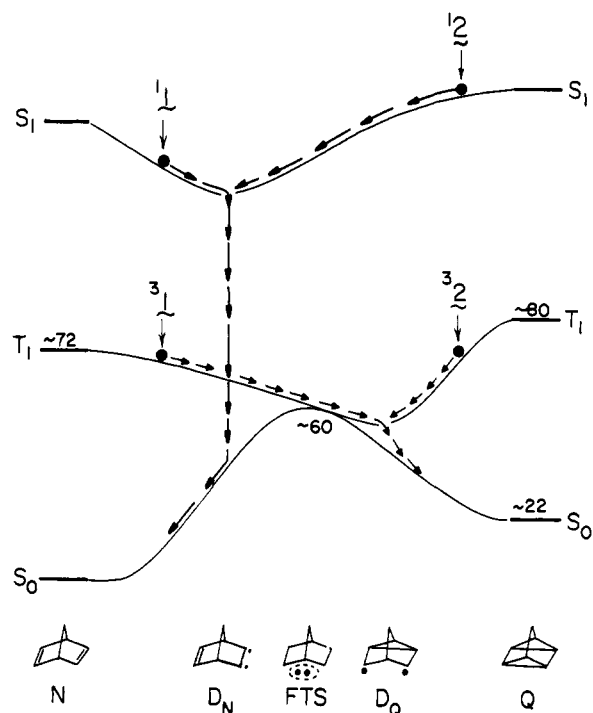
**Figure 1.** Postulated energy surfaces for the interconversion of norbornadiene and quadricyclene.

*delivers singlet diradicals preferentially to N and that the excited triplet surface possesses a minimum which delivers triplet diradicals preferentially to Q.*

Within the theoretical framework of forbidden pericyclic reactions[8-10] we can ask what are the geometries corresponding to the minima on the $S_1$ and $T_1$ surfaces which operate as entries to $S_0$ and what is the nature of the mechanisms by which diradicals are converted to product molecules via these funnels.[9a] We deduce the geometries corresponding to the minima in $S_1$ and $T_1$ as follows. As a first approximation the $D_Q$ species (a 1,3 diradical) possesses a greater average electron separation than the $D_N$ species (a 1,2 diradical). Singlet hydrocarbon diradicals tend to possess wave functions composed of ionic terms (i.e., paired two-electron terms) and to favor a "tight" nuclear geometry to obtain maximum electronic stabilization.[9,11] In contrast, triplet diradicals tend to possess covalent wave functions and to favor "loose" geometries which minimize spatial overlap of the half-filled orbitals.[9,11] Applying these ideas to structures $D_Q$ and $D_N$, we anticipate that the energetically favored geometry (minimum) on the singlet surface for interconversion of N and Q will correspond to structure $D_N$ (a "tight" 1,2 diradical), whereas the energetically favored geometry on the triplet surface (minimum) will correspond to structure $D_Q$ (a "loose" 1,3 diradical). In other words, *we propose that the minimum on the $S_1$ surface, starting from N or Q (and from 1 or 2), will resemble the $D_N$ structure, and the minimum on the $T_1$ surface, starting from N or Q (or from 1 or 2), will resemble the $D_Q$ structure.*

The $D_N$ and $D_Q$ structures may now be related[12] to the "forbidden" (diradicaloid) transition-state structure (FTS) for the symmetry forbidden $_\pi 2_s + _\pi 2_s$ interconversion of N and Q; i.e., the geometry of the FTS is intermediate to that of $D_N$ and $D_Q$ (Figure 1). The mechanism of relaxation through the "funnel" corresponding to structures $D_N$ and $D_Q$ may be electronic, vibrational, spin, or dynamic in origin. Dynamic effects are unlikely since preparation of molecules at various geometries on the $S_1$ or $T_1$ surfaces lead to similar product distributions; i.e., the inherent partitioning ratio to N and Q does not depend strongly on the direction of approach to the funnel. On the $S_1$ surface decay to $S_0$ to form structures re-

sembling norbornadiene will be favored since the $S_1$ funnel lies to the left ("N side") of the FTS structure.

On the $T_1$ surface intersystem crossing is required to deliver the diradical $^3D_Q$ to $S_0$. The rate of spin-orbit-induced intersystem crossing is related to the orientation and overlap of the half-filled orbitals involved in the singlet–triplet interconversion. According to Salem's rules[11] the orbitals of $D_Q$, because of their cant relative to one another, are well suited for rapid intersystem crossing (Scheme I). As a result, the conversion of $^3D_Q$ to $S_0$ should occur most efficiently at geometries to the right of the FTS structure. Thus, we conclude that *both* the geometry of the minimum of the $T_1$ surface *and* the enhanced spin-orbit coupling enjoyed by molecules possessing this structure will favor conversion of triplet diradicals to Q.

The reported[4a,12,13] photochemistry of the parent hydrocarbons N and Q are splendidly consistent with expectations based on the surfaces of Figure 1. For example, the quantum yield for direct photochemical excitation[12] or singlet sensitized excitation[13] of N leads to Q with very low efficiency, results which are consistent with a funnel which delivers excited singlet molecules selectively to $S_0$ with formation of N. Importantly, singlet sensitized excitation[13] of Q results in formation of N, a result which is consistent with passage of singlet molecules (that start with a structure similar to Q or $D_Q$) to the funnel in $S_1$ which delivers molecules to $S_0$ with formation of N. Finally, the photostationary mixtures[4a] of N and Q produced with triplet sensitizers are rich in Q and the quantum yield for triplet photosensitized rearrangement of N to Q is close to unity.[13] These results are consistent with a funnel in the $T_1$ surface that delivers triplets specifically to Q on the $S_0$ surface.

The exclusive formation of N from thermolysis of **2** is unexceptional based on literature precedent.[6e] The process may be a concerted $_\sigma 2 + _\sigma 2 + _\sigma 2$ process and not yield a diradical at all. The small yield of Q from thermolysis of **1** is significant,[2] since the thermal loss of $N_2$ from **1** may produce a singlet *ground-state* diradical close to the geometry of $D_N$ on the $S_0$ surface. The fate of the radical will be determined by whether molecules generated with this geometry slide down the slope leading to N or to Q.

In summary, the cyclic azoalkanes **1** and **2** have been employed to generate the diradicaloid structures $D_N$ and $D_Q$ on the $S_1$ and $T_1$ surfaces corresponding to the interconversion of N and Q. A theoretical interpretation of the results suggests that the $D_N$ structure is a minimum (funnel) on the $S_1$ surface while the $D_Q$ structure is a minimum (funnel) on the $T_1$ surface. Assuming the pertinent surfaces are those corresponding to the orbitally forbidden thermal interconversion of N and Q, it is clear that the funnels $^1D_N$ and $^3D_Q$ should lead preferentially to N and Q, respectively. Furthermore, intersystem crossing should be effective in assisting the conversion of $^3D_Q$ to Q.

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= 0.91), and that conversion of Q → N may also be photosensitized: (a) G. S. Hammond, P. Wyatt, C. D. deBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964); (b) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).

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(7) In general, it appears that near room temperature the $S_1 \rightarrow T$ intersystem crossing in cyclic azoalkanes is inefficient.[5e,f,g] Recent evidence[8] indicates that this inefficiency may be strongly temperature dependent if chemical processes leading to deactivation of $S_1$ are thermally activated, since the rate of intersystem crossing is generally temperature insensitive. Such appears to be the case for **1** and **2** (see temperature effects in Table I).

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## Intramolecular Pericyclic Reactions of Acetylenes. 7.[1] Concertedness of Acetylenic Retro-ene Reactions. Preparation of Optically Active Phenylallene-*3-d*

*Sir:*

Although acetylenic bonds frequently participate in intramolecular reactions whose olefinic analogues are believed to proceed via cyclic six-membered transition states, the ground-state linearity of the acetylenic system raises doubts about the concert of such reactions. We wish to report that stereochemical integrity is preserved in an acetylenic retro-ene reaction as further evidence for concertedness in that reaction, and that we have used this process to generate the first reported allene which is optically active by virtue of isotopic substitution.[2]

As part of our continuing study of the thermal behavior of acetylenic compounds, we have examined the thermolyses of a number of propargylic ethers.[3] Normally the products are those to be expected from a retro-ene cleavage, and the kinetic parameters for about 25 compounds are those to be expected from a concerted process, with $E_a$ ranging from 36 to 42 kcal/mol and $\Delta S^{\ddagger}$ from −6 to −13 eu.[4]
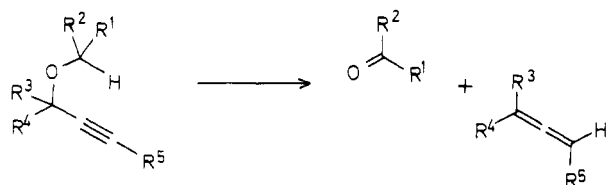


The stereospecificity of concerted, intramolecular rearrangements has been used previously to generate two allenic derivatives of predictable absolute configuration from optically active acetylenic precursors: an acetylenic Claisen rearrangement provided an allenic aldehyde[5] and the $S_{N}i'$ reaction of thionyl chloride on a propargylic alcohol gave a chloroallene.[6] It has been suggested that acetylenic retro-ene reactions proceed via a concerted planar transition state which maximizes orbital overlap of participating bonding systems.[7] If such be the case, then (*R*)-phenylallene-*3-d* (**1**) should be produced from the thermolysis of the trideuteriomethyl ether of (*S*)-1-phenylprop-2-yn-1-ol (**2**).



"S" Configuration                    "R" Configuration
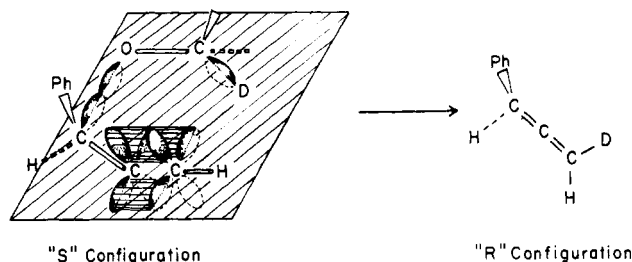
The choice of the phenyl group as a substituent is dictated by the following factors: 1-phenylprop-2-yn-1-ol (**3**) is commercially available (Farchan Division, Chemical Samples Co.), its resolution has been reported,[8] and the presence of the polarizable phenyl substituent provides enhanced optical rotation in the case of isotopic substitution at sp³-hybridized carbon atoms.[9]

The resolution[10] of **3** is outlined in Scheme I. Reaction of racemic **3** with 3-nitrophthalic anhydride (3-NPA) provided the racemic half-acid-ester **4**. Treatment of (±)-**4** with cinchonine led to the precipitation of a crystalline salt, a sample of which was recrystallized from $CHCl_3/MeOH$ to constant melting point, 185–186 °C.[11] Hydrolysis with dilute aqueous HCl provided (−)-**4**, $[\alpha]^{25}_D$ −53.9° (*c* 2.17), mp 152–155 °C. Treatment of the active ester with $LiAlH_4$ gave (−)-**3**, $[\alpha]^{22}_D$ −27.1° (*c* 2.42). The optical purity of this sample was essentially 100% as determined by use of the chiral NMR shift reagent, Eu(hfc)₃,[12] which cleanly separated the resonance lines due to the benzylic protons of the two enantiomeric components in a sample of racemic **3**. Etherification of (−)-**3** with NaH and $CD_3I$ provided the desired trideuteriomethyl ether,[13] (−)-**2**, $[\alpha]^{25}_D$ −42.8° (*c* 1.08). Since the chiral shift reagent did not separate the benzylic protons of **2**, a sample of the same batch of alcohol, (−)-**3**, used to prepare the deuterated either, was converted via the identical procedure, but using $CH_3I$, into the corresponding protio ether.[13] The application of Eu(hfc)₃ indicated less complexation with the ether, but the methyl signal in racemic protio-**2** was cleanly divided into two singlets. Since no trace of one of these singlets could be detected in the spectrum of the active protio ether, its optical purity is also essentially 100% and the Williamson etherification does not lead to any detectable racemization.

The positive antipode of **4** could be obtained from the mother liquor, after removal of the precipitated crystalline cinchonine salt, by treatment with dilute HCl. Reduction of the half-ester with $LiAlH_4$ gave (+)-**3**, but with an optical purity of only ~65% as determined with Eu(hfc)₃. Since cinchonidine is an epimer of cinchonine, it was hoped that use of the former as a resolving agent might lead to a higher optical purity of (+)-**3**. True to expectation, treatment of (±)-**4** with cinchonidine also produced a crystalline salt, which was recrystallized from $CHCl_3/MeOH$, mp 175–177 °C, and was then hydrolyzed with aqueous HCl to yield (+)-**4**, $[\alpha]^{25}_D$ +52.5° (*c* 0.83), mp 155–166 °C. Treatment of (+)-**4** with $LiAlH_4$ gave (+)-**3**, $[\alpha]^{25}_D$ +27.0° (*c* 1.35), which represents optically pure material based on the specific rotation of optically pure (−)-**3**.