migratory aptitude of β-alkyl groups in β-peroxylactones follows the ease of alkoxy radical fragmentation, i.e., *i*-Pr > Et > Me > Ph,[2b] indicating that the driving force for rearrangement is alkoxy center dominated. These facts corroborate the suggestion that the 1,5 diradical $^{\mathrm{S}}\mathbf{2\pi}$ is very selective in its chemical behavior.

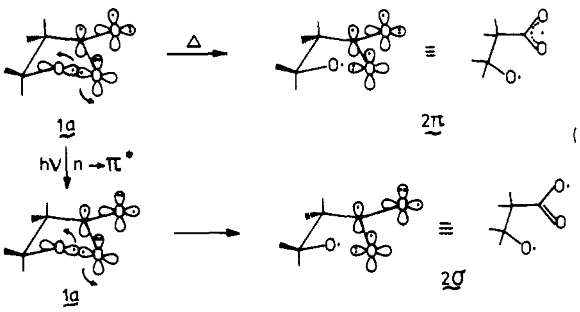
The fate of the triplet state σ-type 1,5 diradical $^{\mathrm{T}}\mathbf{2\sigma}$ is also quite well defined since the TMD chemienergized process (fact ii; cf. entry 2 in Table I) affords exclusively oxirane **5a** via triplet acetone sensitization. Whether $^{\mathrm{T}}\mathbf{2\sigma}$ relaxes into the more stable $^{\mathrm{T}}\mathbf{2\pi}$ 1,5 diradical or whether it directly decarboxylates into the 1,3 diradical **4** cannot be differentiated on the basis of our results. The disadvantage of a π-type 1,5 diradical $^{\mathrm{T}}\mathbf{2\pi}$ is that decarboxylation should be more difficult. However, it is clear from previous stereolabeling experiments[3] that the 1,3 diradical is the immediate precursor to the oxirane product.

The most complex behavior is exhibited by the singlet-state σ-type 1,5 diradical $^{\mathrm{S}}\mathbf{2\pi}$, which is formed in the direct photolysis (fact iii; cf. entry 3 in Table I) and the acetone-sensitized photolysis (fact iv; cf. entry 4 in Table I) via the singlet excited β-peroxylactone $^{\mathrm{S}}\mathbf{1a}^{*}$. Since in the *acetone-sensitized photolysis increasing β-peroxylactone concentration leads to proportionally more pinacolone vs. oxirane product (cf. footnote f in Table I)*, it appears that the β-peroxylactone is an effective quencher of singlet excited acetone in order to intervene with the efficient intersystem crossing to triplet excited acetone.

Why do we need to propose a singlet-state σ-type 1,5 diradical $^{\mathrm{S}}\mathbf{2\sigma}$ as an intermediate? The direct photolysis and acetone-sensitized photolysis lead to pinacolone, oxirane, and acetone products. Since the pinacolone is $^{\mathrm{S}}\mathbf{2\pi}$ derived and the oxirane $^{\mathrm{T}}\mathbf{2\sigma}$ derived, for the direct photolysis we need a branching point in our mechanism to interconnect these intermediates. The branching point must come after the intersystem-crossing step $^{\mathrm{S}}\mathbf{1a}^{*} \rightarrow {}^{\mathrm{T}}\mathbf{1a}^{*}$ since the direct photolysis in the presence of the triplet-state quencher piperylene did not alter the product composition (facts iii and v; compare entries 3 and 5 in Table I). The new intermediate representing this branching point must be able to relax into the stabilized singlet-state π-type 1,5 diradical $^{\mathrm{S}}\mathbf{2\pi}$ to account for pinacolone product, it must either intersystem cross to the triplet-state σ-type 1,5 diradical $^{\mathrm{T}}\mathbf{2\sigma}$ or decarboxylate into the 1,3 diradical **4** to account for the oxirane product, and it must be able to fragment into acetone and presumably α-lactone product. The most probable candidate that in our opinion embodies all these requisites is the singlet-state σ-type 1,5-diradical $^{\mathrm{S}}\mathbf{2\sigma}$, an electronic isomer of the more stable $^{\mathrm{S}}\mathbf{2\pi}$ species.[7]

To suppose that the singlet excited β-peroxylactone $^{\mathrm{S}}\mathbf{1a}^{*}$ in the direct photolysis decarboxylates in part into the 1,3 diradical **4** in order to account for the oxirane product and in part affords a singlet 1,5 diradical **2** (without distinction of σ- and π-type electronic configurations) would require a similar behavior for the triplet excited β-peroxylactone $^{\mathrm{T}}\mathbf{1a}^{*}$ in the TMD chemienergized process. However, only oxirane product is formed in the latter case (fact ii; cf. entry 2 in Table I). It appears to us that the above mechanistic premise, which was the one we originally proposed,[2,3] should afford pinacolone, oxirane, and acetone products in the TMD chemienergized process.

As to the question of why the thermal and photochemical activation processes of β-peroxylactone **1a** lead to 1,5 diradicals of distinct electronic configurations, i.e., **2π** and **2σ**, cogent arguments are presented in the orbital diagrams of eq 2. In the thermal mode, the already tense five-membered ring, shown in the conformation with an optimal dihedral angle of the peroxide bond, must shear apart rather than stretch apart the oxygen atoms, as indicated by the arrows. This vibrational motion seems to be quite suitable to overlap the odd-electron orbital with the carbonyl bond in generating a **2π**-type 1,5 diradical. On the other hand, the photochemical mode appears to be n,π* derived.[8] Consequently, suitable line up of the odd-electron orbital that is developing at the carboxylate oxygen through the twisting mode in the n,π* excited **1a** leads to the **2σ**-type 1,5-dioxyl radical.



(2)

Although other mechanistic interpretations are possible, our suggestion that a common 1,5 diradical, but of distinct electronic configuration, intervenes in the thermal and photochemical decarboxylation of β-peroxylactones is an attractive and internally consistent rationalization of our unusual results. It would be more reassuring if we could provide direct evidence for the 1,5 diradical in the photochemical process. Such experiments are difficult, but attempts along these lines are being presently pursued.

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References and Notes

(1) Part No. 91 in the Cyclic Peroxide Series.
(2) (a) Adam, W.; Cueto, O.; Guedes, L. N.; Rodriguez, L. O. *J. Org. Chem.* **1978,** *43*, 1466. (b) Adam, W.; Cheng, Y.-M. *J. Am. Chem. Soc.* **1969,** *91*, 2109. (c) Adam, W.; Cheng, Y.-M.; Wilkerson, C.; Zaidi, W. A. *Ibid.*, **1969,** *91*, 2111. (d) Adam, W.; Wilkerson, C. *Chem. Commun.* **1971**, 1569.
(3) Adam, W.; Santiago Aponte, G. *J. Am. Chem. Soc.* **1971,** *93*, 4300.
(4) Turro, N. J.; Lechtken, P. *J. Am. Chem. Soc.* **1972,** *94*, 2886.
(5) Kochi, J. K. In "Free Radicals", Kochi, J. K., Ed., Wiley, New York, 1973, Vol. 2, Chapter 23.
(6) (a) Koenig, T.; Wielesek, R. A.; Huntington, J. G. *Tetrahedron Lett.* **1974,** 2283. (b) Hoobler, J. A. Doctoral Dissertation, University of Oregon, 1972.
(7) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978,** *11*, 381.
(8) Photoelectron spectroscopy shows that the lowest energy ionization is out of the carbonyl oxygen lone pair. We are grateful to Professor R. Gleiter (Heidelberg) for this measurement.
(9) NIH Career Development Awardee, 1975–1980.

Waldemar Adam,*[9] Omar Cueto, Luis N. Guedes
Department of Chemistry, University of Puerto Rico
Rio Piedras, Puerto Rico 00931

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2,3-Benzobicyclo[2.2.2]oct-2-ene-5,7-diyl Diradical as a Common Intermediate in the Di-π-methane Rearrangement of 6,7-Benzobicyclo[3.2.1]octa-2,6-diene and the Denitrogenation of the Corresponding Tricycloazoalkane

Sir:

The ubiquitous di-π-methane reaction has been one of the fascinating photorearrangements, both for mechanistic and synthetic investigations.[1] For example, 6,7-benzobicyclo[3.2.1]octa-2,6-diene (**1**) rearranges into 3,4-benzotricyclo[3.2.1.$0^{2,2}$]oct-3-ene (**2**) on direct (254 nm) or acetone-sensitized (300 nm) photolysis, presumably via the postulated diradicals **3** and **4** (eq 1).[2] Recently it has been shown[3] that

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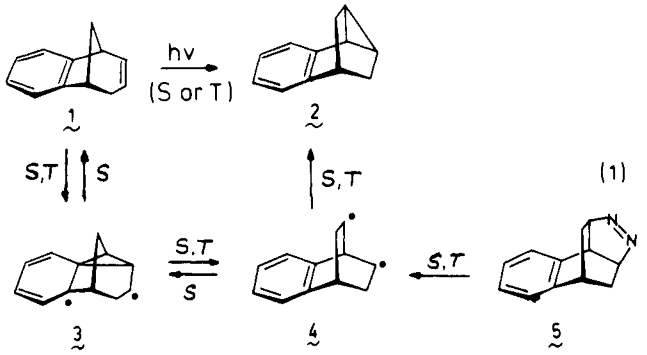

nitrogen extrusion from polycyclic azoalkanes represents an effective route for the independent generation of such diradical intermediates and thereby validates the mechanism of these photorearrangements. Through our novel dipolar cycloaddition[4] of *N*-phenyl-1,2,4-triazoline-3,5-dione to strained bicycloalkenes as **1**, we prepared the tricyclic azoalkane **5**,[5] which provides a convenient entry into the diradical manifold postulated for the di-π-methane rearrangement of **1**. From our results (Table I) [i.e., (i) thermolysis and direct photolysis afford both **1** and **2**; (ii) benzophenone-sensitized photolysis and tetramethyl-1,2-dioxetane (TMD) chemienergization give only **2**], we confirm that the diradicals **3** and **4** are indeed intermediates in the ground-state and singlet and triplet excited-state reactions of azoalkane **5** and, therefore, also in the di-π-methane reaction of bicycloalkene **1**. Herein we report the details of this investigation.

The thermolysis of azoalkane **5** was carried out by subliming it through a 20-cm-long hot tube at ~350 °C and 0.2 Torr, collecting the affluent in a dry ice cold trap. Quantitative VPC analysis gave the results shown in Table I. A control experiment revealed that the tricycloalkene **2** did not isomerize into bicycloalkadiene **1** under these vacuum flash pyrolysis conditions. These results suggest that on thermal activation the azoalkane **5** loses N_2 to afford initially the singlet diradical **4**. The latter predominantly collapses into tricycloalkene **2**, but a significant fraction of diradical **4** isomerizes into the bicycloalkadiene **1** via the cyclopropyldicarbinyl diradical **3**. Consequently, the thermal denitrogenation of azoalkane **5** connects with the di-π-methane rearrangement through the diradicals **3** and **4**, of which the latter constitutes an energy minimum (a "funnel")[6] on the singlet ground-state energy surface of the $\mathbf{5} \rightarrow \mathbf{2} + \mathbf{1}$ transformation.

The direct photolyses (Table I) were carried out in a Rayonet photoreactor, supplied with 350- (n,π^* excitation of azo chromophore) and 254-nm (π,π^* excitation of benzene chromophore) lamps, using 0.041 M solution in *n*-pentane and Pyrex and quartz vessels, respectively. Again both **1** and **2** were formed, the latter as major product. Control experiments confirmed that under the direct photolysis conditions **1** was isomerized into **2**. Therefore, these photolyses were carried out below 5% photoconversion of azoalkane **5**. We conclude that the singlet excited azoalkane **5**, irrespective whether the azo or benzene chromophores are engaged, extrudes nitrogen to afford first the singlet diradical **4**. Subsequently diradical **4** either collapses into **2** (major route) or rearranges into **1** via diradical **3** (minor route). Also in the direct photolysis of azoalkane **5**, diradical **4** constitutes an energy minimum.

The triplet-sensitized photolysis was carried out also in a Rayonet photoreactor, which was equipped with 300-nm lamps, irradiating a solution of 0.01 M **5** and 0.1 M benzophenone in *n*-pentane in a Pyrex vessel, which was protected with a $K_2Cr_2O_7/K_2CO_3$ filter[3a] to allow to pass only radiation in the 300-330-nm region. Under these carefully controlled conditions only the tricycloalkene **2** was formed. Control experiments showed that the VPC detection limit of bicycloalkadiene **1** was ~0.01%. Furthermore, under these photolysis conditions the di-π-methane reaction $\mathbf{1} \rightarrow \mathbf{2}$ is inefficient.[2b] Thus, **1** is not formed in the triplet-sensitized denitrogenation of azoalkane **5**. Consequently, the triplet diradical **4** prefers to cyclize into tricycloalkene **2** rather than rearrange into bicycloalkadiene **1** via diradical **3**. This is in contrast with the triplet-sensitized di-π-methane reaction of bicycloalkadiene **1**, which does afford the tricycloalkene **2**, albeit in ca. one-tenth the efficiency of the singlet-state reaction,[2b] via the triplet diradical rearrangement $\mathbf{3} \rightarrow \mathbf{4}$.

Table I. Product Yields of the Thermolysis and Photolysis of Azoalkane **5**

process	conditions	% yields[a]	
		1	**2**
thermolysis	gas phase, ~350 °C	18 ± 1	82 ± 2
direct photolysis	*n*-pentane, 350 nm, Pyrex	18 ± 1	82 ± 1
direct photolysis	*n*-pentane, 254 nm, quartz	9 ± 3	91 ± 3
sensitized photolysis	*n*-pentane, 300 nm, $Ph_2C{=}O$, Pyrex	*b*	100
TMD-chemienergization	toluene, 80-85 °C, 2 h	*b*	100

[a] Determined by quantitative VPC (flame ionization) using a 6 ft × 1/8 in. stainless steel column packed with 10% SE-30 on Chromosorb P and operated at injection and detector temperatures of 250 °C and a column temperature program of 16 °C/min starting at 60 °C and finishing at 220 °C and a carrier gas flow of 20 mL/min. [b] Below VPC detection limit (~0.01%).

The tetramethyl-1,2-dioxetane (TMD) chemienergization[7] was conducted by heating a solution of 0.02 M **5** and 0.1 M TMD in toluene in a sealed tube at ~80-85 °C for 2 h. Quantitative VPC analysis revealed ~40% conversion of azoalkane **5** exclusively into tricycloalkene **2**. Control experi-

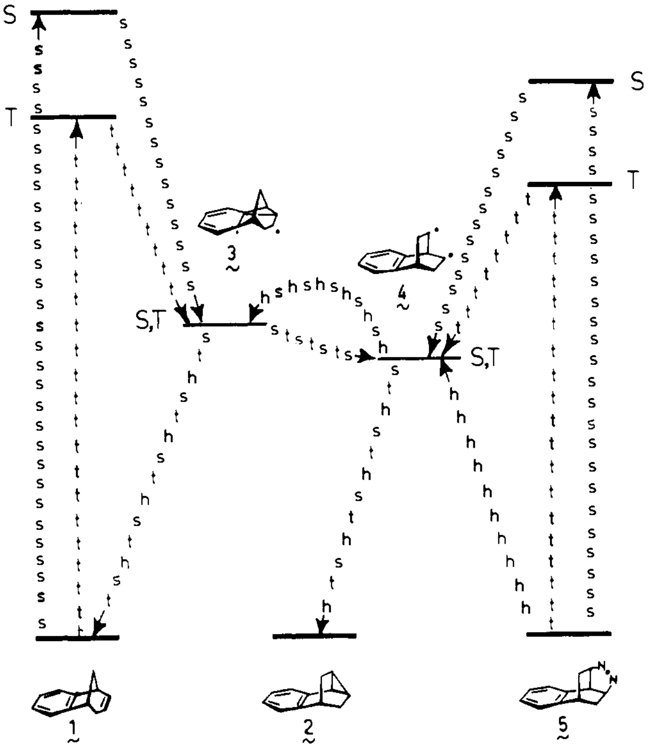

Figure 1. Qualitative energy diagram interconnecting the thermal (h h h), singlet (s s s), and triplet (t t t) excited-state denitrogenations of azoalkane **5** with the singlet (s s s) and triplet (t t t) excited-state di-π-methane rearrangements of bicycloalkadiene **1** into tricycloalkene **2** via the cyclopropyl dicarbinyl **3** and bicyclo[2.2.2]octenediyl **4** diradicals.

ments again confirmed less than ~0.01% bicycloalkadiene **1** formation as upper limit. Thus, the triplet-state acetone, which is formed in the thermolysis of TMD, sensitizes the decomposition of azoalkane **5** affording only tricycloalkene **2** via the triplet diradical **4**. This is in complete concordance with the benzophenone-sensitized photolysis of azoalkane **5**.

In Figure 1 we attempt to summarize the thermal, direct, and triplet-sensitized photolytic and the TMD-chemienergized denitrogenation of azoalkane **5** and the direct and triplet-sensitized photolytic di-π-methane reaction of bicycloalkadiene **1** in terms of a composite energy diagram. The key features of this qualitative picture are the interconverting cyclopropyldicarbinyl diradical **3** and the bicyclo[2.2.2]octenediyl diradical **4**, which provide a useful mechanistic interconnection between the di-π-methane process **1** → **2** and the denitrogenation process **5** → **1** + **2**.

Work is in process to acquire the essential activation parameters and photophysical data to place this mechanistic diagram on a quantitative basis. In the accompanying communication we describe a similar study on the di-π-methane rearrangement of benzonorbornadiene, using the corresponding azoalkane as source for the postulated diradicals.

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References and Notes

(1) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973,** *73,* 531. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967,** *89,* 3932.

(2) (a) Hahn, R. C.; Rothman, L. J. *J. Am. Chem. Soc.* **1969,** *91,* 2409. (b) Goldschmidt, Z.; Gutman, U. *Tetrahedron* **1974,** *30,* 3331. (c) Hahn, R. C.; Johnson, R. P. *J. Am. Chem. Soc.* **1977,** *99,* 1508.

(3) (a) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976,** *98,* 7680. (b) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *Ibid.* **1976,** *98,* 4320. (c) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J., *Ibid.* **1977,** *99,* 7388.

(4) (a) Adam, W.; De Lucchi, O.; Erden, I. *Angew. Chem.* **1979,** *91,* 4735. (b) Adam, W.; De Lucchi, O. *Tetrahedron Lett.* **1979,** 4367.

(5) The details for the preparation of azoalkane **5** will be reported separately as part of a general procedure on this novel rearrangement.

(6) (a) Michl, J. *Photochem. Photobiol.* **1977,** *25,* 141. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969,** *91,* 3316. (c) Zimmerman, H. E. *Ibid.* **1966,** *88,* 1566.

(7) Adam, W.; Cheng, C.-C.; Cueto, O.; Sakanishi, K.; Zinner, K. *J. Am. Chem. Soc.* **1979,** *101,* 1324.

(8) NIH Career Development Awardee, 1975–1980.

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Waldemar Adam,*[8] Nestor Carballeira,[9] Ottorino De Lucchi
Department of Chemistry, University of Puerto Rico
Rio Piedras, Puerto Rico 00931

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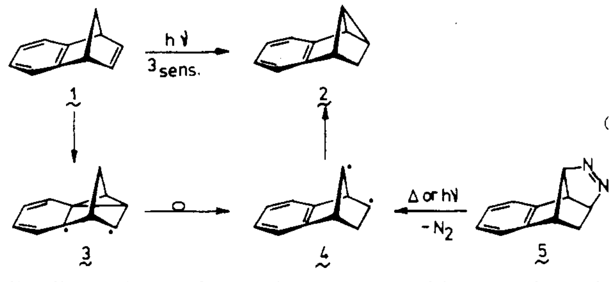
Unusual Thermal and Photochemical Transformations of the Azoalkane 2,3-Diaza-7,8-benzotricyclo[4.3.0.0^{4,9}]nona-2,7-diene

Sir:

The use of cyclic azoalkanes for the thermal and photolytic generation of diradicals is well documented.[1] Recent fascinating examples include the formation of the prismanyl,[2] the norbornadienyl and quadricyclenyl,[3] and the barrelenyl diradicals[4] via denitrogenation of the respective azoalkane precursors. The chemical behavior of these diradicals, some of which have been postulated as reaction intermediates in the general di-π-methane rearrangement of the corresponding hydrocarbons, has provided in-depth understanding of the mechanistic details of this ubiquitous photorearrangement. The preceding communication reports such a study.

An exhaustively studied di-π-methane rearrangement is the triplet-sensitized photocyclization of benzonorbornadiene (**1**) into 2,3-benzotricyclo[2.2.1.0^{5,7}]hept-2-ene (**2**), formed by the collapse of the ultimate diradical **4**, which results from the initial diradical **3** (eq 1).[5,6] For mechanistic conformation, the diradical **4** has so far not been generated by an independent route.



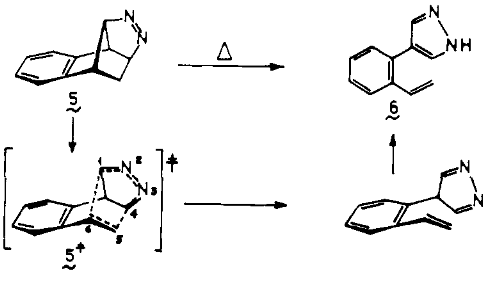
(1)

Recently[7] we succeeded in preparing the tricyclic azoalkane **5**, which on thermal or photochemical extrusion of molecular nitrogen, should provide a convenient entry into the diradical manifold of this di-π-methane rearrangement. Therefore, we have investigated the thermolysis and photolysis of azoalkane **5**, following the modus operandi outlined in the preceding communication, but uncovered some unprecedented chemical behavior of this unusual azoalkane. The highlights of our results are (i) on thermolysis (eq 2) **5** isomerizes quantitatively into 4-(2′-styryl)pyrazole (**6**); (ii) on direct photolysis (eq 1) **5** extrudes N_2 quantitatively, affording mainly the tricycloalkane **2** and some norbornadiene (**1**); (iii) on benzophenone-sensitized photolysis (eq 3) **5** rearranges into 2,3-diaza-7,8-benzotricyclo[4.3.0.0^{2,9}]nona-3,7-diene (**7**).

This unusual thermal and photochemical behavior of azoalkane **5**, especially if contrasted with the more normal comportment of the next higher azoalkane homologue reported in the previous communication, provides a unique opportunity for broadening the scope and understanding of the chemistry of azoalkanes. Below we summarize the experimental evidence and their mechanistic interpretations on this study.

On vacuum flash pyrolysis of the azoalkane **5** by sublimation at 60 °C and 0.2-0.3 Torr through a hot tube maintained at ~400 °C and collection of the affluent in an ice-cooled trap afforded a quantitative yield of the pyrazole **6**, mp 114 °C, $C_{11}H_{10}N_2$ elemental composition by combustion analysis, *m/e* 170. The following spectral data[8] confirm the structural assignment: ^{1}H NMR (CCl_4, Me_4Si) δ (ppm) 5.10-7.15 (3 H, $CHCH_2$, ABC pattern, $J_{AB} = 1.5$, $J_{BC} = 10.06$, $J_{AC} = 16.15$ Hz), 7.65 (2 H, pyrazole, s), 7.1-7.7 (4 H, C_6H_4, m), 10.4 (1 H, N-H, br s); ^{13}C NMR ($CDCl_3$, Me_4Si) δ (ppm) 115.34, 120.80, 126.38, 127.08, 127.81, 129.52, 131.23, 133.56, 136.22; IR (KBr) ν (cm^{-1}) 3150, 3080, 2980, 1480, 1380, 1150, 1040, 1000, 960, 920, 875. On catalytic hydrogenation over Pd/C, 1 mol of H_2 was absorbed, resulting quantitatively in 4-(2′-ethylphenyl)pyrazole, mp 102.5 °C, $C_{11}H_{12}N_2$ elemental composition by combustion analysis; the ^{1}H NMR confirmed the replacement of the vinyl for the ethyl pattern.

We interpret this unexpected thermal behavior of the azoalkane **5** in terms of the retro-Diels–Alder process, followed by tautomerization, as shown in eq 2. Apparently the C_1-C_6



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