Table I. Comparison of Product Quenching and Flash Data for the Reaction of **1** with Alkenes

solvent	quencher[a]	$k_a\tau$,[b] M^{-1}	k_q,[c] $M^{-1}\,s^{-1}$	τ_T,[c] ns	$k_q\tau_T$	ϕ[d]
AN	TME	0.48	$<2 \times 10^6$	27	<0.05	0.041 (0.25)
IPA	TME	0.45	$<2 \times 10^6$	33	<0.06	
AN	CP	0.43	$\leq 1.4 \times 10^6$	27	≤0.05	0.032 (0.34)
IPA	CP		$\sim 1 \times 10^7$	33	~0.3[e]	
isooctane	CP		$<1 \times 10^6$	24	≤0.02	
AN	DME	1.2	$<1 \times 10^6$	27	<0.03	(0.44)
IPA	DME		$<3 \times 10^6$	33	<0.08	
AN	CH	0.13	$<2 \times 10^6$[f]	27	<0.05	
IPA	CH	0.39[g]	$<2 \times 10^6$[f]	33	<0.06	

[a] TME = tetramethylethylene; CP = cyclopentene; DME = 1,1-dimethoxyethylene; CH = cyclohexene. [b] From product quenching studies. [c] From flash studies. [d] Quantum efficiencies for cycloaddition at 313 nm of 0.2 M enone at 1.0 M alkene and neat alkene (in parentheses). [e] The apparent quenching observed in this case may be due to solvent effects. [f] From ref 13 and: Dunn, D. A. Ph.D. Dissertation, New York University, 1985. [g] Reference 5.

I are similar in magnitude to those previously reported[8,17] for photoaddition of alkenes to cyclohexenones. The unavoidable conclusion is that the species intercepted by alkenes on photoexcitation of **1** is not the reactive enone triplet, i.e., that at least for these systems the Corey–de Mayo photoannelation mechanism does not apply.

In the correct form of the mechanism, shown in Scheme II, the enone π,π^* triplet is a precursor of a reactive intermediate I, which proceeds to lumiketone or reverts to starting material. In the absence of alkene, the reversion predominates, since rearrangement efficiencies are typically on the order of 0.01,[10b,18] while photocycloaddition efficiencies are as high as 0.44 in neat alkene. The Corey–de Mayo mechanism would require a substantial reduction in τ_T at high alkene concentrations, which is not observed in the flash experiments nor in steady-state quenching by naphthalene of photocycloaddition of TME to **1** in IPA. Finally, relative reactivities of 17 alkenes as quenchers of rearrangement of **1** show no correlation with ionization potentials,[19] as would have been expected for formation of an enone–alkene exciplex.[20] Rather, alkene reactivity seems to be governed mainly by steric parameters.

We suggest that I may be a ground-state *trans*-cyclohexenone analogous to well-characterized trans isomers of cycloheptenone,[21] cyclooctenone,[22] and 1-phenylcyclohexene.[23] Corey failed to detect such a species by IR spectroscopy upon irradiation of 2-cyclohexenone in a hydrocarbon matrix at −190 °C.[21a] A *trans*-cyclohexenone was implicated by Hart in the photoaddition of methanol to Pummerer's ketone,[24] a process which occurs in very low yields in the case of **1**.[25] The suggestion that I is on the ground-state rather than the triplet-state potential surface is supported by the low value of log A (8.01 ± 0.15) measured for decay of $^3\mathbf{1}^*$ in isooctane ($E_a = 0.52 \pm 0.16$ kcal/mol), inconsistent with adiabatic isomerization of $^3\mathbf{1}^*$ but compatible with intersystem crossing to the ground-state surface.

A corollary of our findings (see Scheme I) is that the photorearrangement of **1** to **2** appears to occur on the ground-state potential surface rather than directly from an enone triplet as long held.[5,8c,10,26] This would provide an explanation for the high stereospecificity and very low quantum efficiency of this reaction,[10] as well as the formation of products attributed many years ago to a "polar-state" intermediate.[27]

As a mechanistic alternative, the Corey–de Mayo mechanism (Scheme I) may hold for cyclopentenones, geometrically constrained cyclohexenones, and perhaps even cyclohexenone itself. Experiments are in progress to examine this possibility.

Acknowledgment. We are grateful for support of this project at NYU through a grant from the National Science Foundation (CHE-8320154).

Registry No. 1, 1073-13-8; TME, 563-79-1; CP, 142-29-0; DME, 922-69-0; CH, 110-83-8.

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Flash Pyrolysis of 1,4-Bis(5-tetrazolyl)benzene. Entry to the C_8H_6 Energy Surface[1,2]

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Twenty years ago Murray and Kaplan,[4] building upon earlier work[5] on polyphenyl bis-diazo compounds, irradiated 1,4-bis(diazomethyl)benzene in benzene and obtained a 2% yield of a diadduct to solvent. They did not claim dicarbene (**1**) as an intermediate, recognizing that a sequence of events in which monocarbenes were the active ingredients was likely. In the succeeding years there have been a number of other reactions in which polycarbenes were possible, if usually unlikely, intermediates.[6] Most impressive has been the recent work in which polycarbenes containing ever growing and quite remarkable

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(1) Support for this work by the National Science Foundation through Grant CHE 83 18345 is gratefully acknowledged.

(2) Portions of this work are taken from the A. B. Theses of J. L. F. and M. E. M., Princeton University, 1978 and 1976.

(3) Current address: Department of Chemistry, University of Queensland, St. Lucia, Brisbane, Australia.

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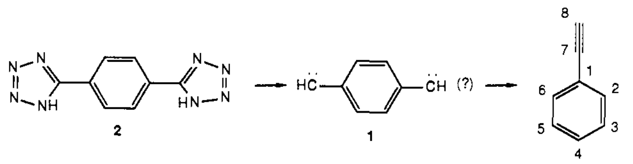
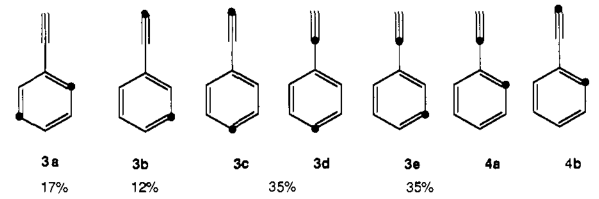
numbers of unpaired electrons have been identified at low temperature by ESR.[7]

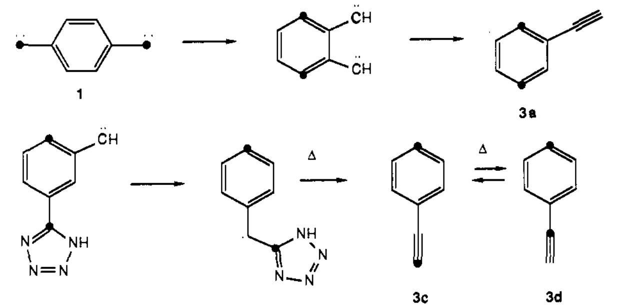
It was our idea to generate dicarbene **1** in the gas phase. Under these conditions there would be greater opportunity for a second carbene to be generated before intermolecular chemistry, so easy in solution, destroyed the first. Although the exact nature of the intermediate we have produced remains difficult to specify in detail, it is clear that we have been able to enter the C_8H_6 energy surface and that new chemistry has been found. As precursor of the hoped-for dicarbene we selected **2**, an effective and safe[8] potential source of **1**. *p*-Di(cyano-^{13}C)benzene was converted to **2** using a modification of the method of Finnegan et al.[9] Pyrolysis of 20% dilabeled **2** at 600 °C (0.01 torr) led to ca. 3% yield[10] of phenylacetylene (25% relative yield), accompanied by <1% (relative) of other hydrocarbons, including toluene, styrene, and xylenes. Rather larger amounts of nitriles are formed,[10] doubtlessly through the known[8] reversal of the tetrazole-forming process. Mass spectrometry showed that the phenylacetylene contained the expected 20% label. The absence of other labeling patterns requires that phenylacetylene be the product of intramolecular chemistry.

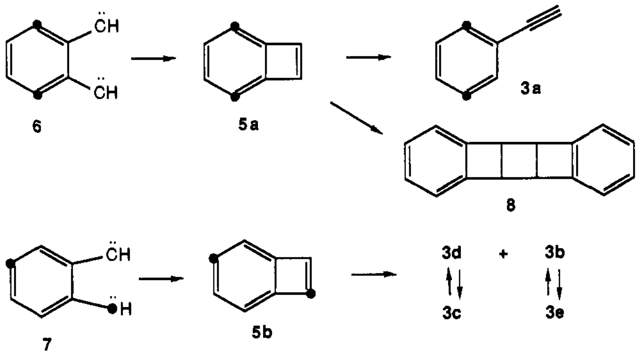


Analysis of the 250- and 500-MHz ^{13}C NMR spectra[11] of phenylacetylene showed that all positions were labeled except for the ipso carbon, C_1. Further analysis of the patterns of the labels revealed that five dilabeled species were present, **3a–e**. In **3a** C_2 is coupled to C_5 by 8.8 Hz, as expected for a para coupling.[12] In **3b** and **3c** C_8 is coupled to C_3 and C_4, respectively, by <0.3 Hz.[12] In **3d** and **3e**, C_7 is coupled to C_4 and C_3 by 1.6 and 5.5 Hz, respectively.[12] The lack of large 1,2 couplings (50–175 Hz for various sp–sp, sp–sp^2, and sp^2–sp^2 couplings)[12] eliminates isomers in which adjacent carbons are labeled and no meta interaction in the ring (expected J = 0.6–3.8 Hz)[12] can be found. Isomers **4a** and **4b**, if present, would be expected to show couplings of 2.6 and 1.7 Hz, respectively.[12]



It now remains to rationalize the five observed isomers. For two ring carbons to be labeled, both tetrazoles must be decomposed before tetravalency is achieved. The key diagnostic compound for such a process is **3a**. Were but one tetrazole to decompose, rearrangement take place, and then phenylacetylene be produced, the labeling pattern must be that of **3c**. But from where do the other isomers arise? In 1974, R. F. C. Brown and his co-workers discovered the remarkable degenerate rearrangment of phenylacetylene[13] which would serve to generate **3d** from **3c**. Compounds **3b** and **3e** are not so simply rationalized, however. We suggest that benzocyclobutadienes are intermediates. Two, **5a** and **5b**, are the potential intramolecular cyclization products of the rearranged dicarbenes **6** and **7** (and/or the monocarbene, monotetrazole related to **7**). Compound **5a** leads only to **3a**, but **5b** must produce both **3b** and **3d**, which, in turn, can undergo the R. F. C. Brown rearrangement to give **3e** and **3c**. The economy of this mechanistic hypothesis which predicts only those isomers observed and no others is attractive, but more compelling is the isolation from the reaction mixture of small amounts (<0.5%) of **8**, one of the known dimers of benzocyclobutadiene.[14]





We have couched our arguments in terms of simple aryl dicarbenes. Just as is the case in the phenylcarbene, C_7H_6 energy surface, the phenyldicarbene, C_8H_6 surface contains many potential intermediates very close in energy.[15] In the former case ab initio calculations[16] place phenylcarbene and nonplanar cycloheptatetraene (**9**) at very similar energies, with planar cycloheptatrienylidene **10** at higher energy. There is compelling spectroscopic evidence that the tetraene is formed first from the ring expansion of phenylcarbene[17] and good experimental evidence that cycloheptatrienylidene is involved in some of the chemistry.[18] A double ring expansion of **1** (or two sequential ring expansions of monocarbenes) would lead to cyclooctapentaene (**11**) which can accommodate all of the labeling results, as well as close to

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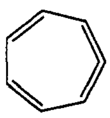
benzocyclobutadiene. Indeed **11** has been suggested as an intermediate in the room temperature conversion of octa-3,5-diene-1,7-diyne to benzocyclobutadiene and, ultimately, its dimers.[19] It seems very likely to us that **1**, **11**, and perhaps dicarbene **12** will all be accessible under our conditions.



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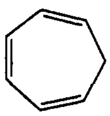

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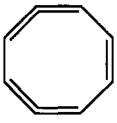

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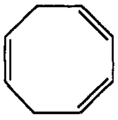

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Registry No. **2**, 6926-49-4.

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Photoinduced Electron-Transfer Fragmentation of Amino Alcohols: Stereochemical Effects and Connectivity between One- and Two-Electron Events

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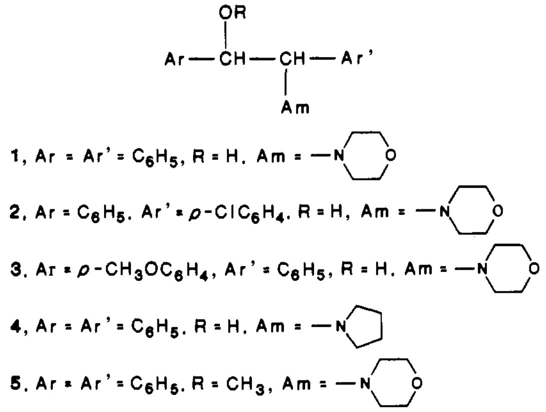
Reactions of radical ions or radical ion pairs formed by photoinduced electron transfer are of considerable current interest.[1–15] Among the possible fates of ions formed by heteroatom oxidations is C–C bond fragmentation.[16–21] Recently we reported that certain tertiary amines suffer C–C bond cleavage when oxidized by acceptors excited by visible light.[22] For amino ketones this reaction was indicated to proceed via homolytic cleavage of the bond between the carbonyl and C_α of the amine to efficiently yield free radicals. Herein we report studies with several β-amino alcohols (**1–4**) which demonstrate that photoredox-induced cleavage of the C_α–C_β bond can be a clean and efficient reaction having close analogy to two-electron solvolytic fragmentations.[23,24] Noteworthy features of the amino alcohol fragmentation are the high chemical specificity of the cleavage, the connectivity between one- and two-electron bond reorganization, and a remarkably large stereochemical effect on reactivity.



$$\text{Ar—}\overset{\text{OR}}{\overset{|}{\text{CH}}}\text{—}\underset{\text{Am}}{\underset{|}{\text{CH}}}\text{—Ar}'$$

1, Ar = Ar' = C_6H_5, R = H, Am =

2, Ar = C_6H_5, Ar' = p-ClC_6H_4, R = H, Am =

3, Ar = p-$CH_3OC_6H_4$, Ar' = C_6H_5, R = H, Am =

4, Ar = Ar' = C_6H_5, R = H, Am =

5, Ar = Ar' = C_6H_5, R = CH_3, Am =

The amino alcohols used in this study were synthesized either by reaction of a secondary amine with the appropriate epoxide (*threo*- and *erythro*-**1** and **4**) or by a sequence of benzoin condensation and chlorination followed by amine substitution and reduction[25] to yield **2** and **3**. The erythro ether **5** was prepared by reaction of *erythro*-**1** with sodium hydride and methyl iodide. The visible light-absorbing electron acceptors, thioindigo (TI) and $Ru[5,5'\text{-}CO_2Et(bpy)]_3(PF_6)_2$ (RuL_3^{2+}), were prepared and purified as reported elsewhere;[26–28] photolyses were carried out with either a 200-W mercury lamp or a tungsten lamp with filters to restrict the exciting light to wavelengths (400–500 nm) absorbed only by the acceptors. Solutions containing the amino alcohol, electron acceptor, and solvent (benzene, methylene chloride, acetonitrile, or acetonitrile–water) were vacuum degassed by freeze–pump–thaw cycles; product analyses of irradiated samples were by HPLC (for amino alcohols and their photolysis products), UV–vis absorption spectroscopy (TI, RuL_3^{2+}, and their reduction products), and gas chromatography. Infrared spectra were obtained on a FT-IR Matson Series 100 spectrometer. NMR studies of photoreacting solutions were carried out on vacuum degassed samples in CD_3CN or C_6D_6 to which a small amount of D_2O (3%) had been added; spectra were measured on a GE-NMR QE-300 spectrometer.

A detailed study of the reaction of **1–3** with TI as the light-absorbing electron acceptor shows an especially clear example of a net two-electron redox fragmentation process occurring according to eq 1. When **1** and TI are irradiated in a NMR tube new proton signals due to the aldehyde hydrogen of benzaldehyde and α_{C-H} of morpholine (ratio 1:2) appear as the photolysis proceeds. When TI is irradiated with **2** or **3**, proton signals for benzaldehyde, Ar'CHO, and the C–H of morpholine appear in the ratio 1:1:4; in all cases no signals due to *N*-benzylmorpholine or other products from the amine can be detected.[29] Irradiation of either RuL_3^{2+} or TI with **2** and **3** in acetonitrile–water or benzene–water leads to the two aldehydes (eq 1) in equal amounts as detected by HPLC.[30] The yields of benzaldehyde from **1** and conversion of

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(29) *N*-Benzylmorpholine exhibits proton signals which are clearly detectable under the reaction conditions.

(30) Although a thorough investigation of solvent effects has not yet been completed, preliminary results indicate that increase in solvent polarity is accompanied by a decrease in reactivity and an increase in diastereomeric selectivity.