evidence from laser flash irradiation of several cyclic enones (including cyclohexenone itself, acetylcyclohexene, and testosterone) for the generation of transient triplet and ground-state species with twisted geometries.[23] Although some other cyclohexenones, most notably the 2-methyl and 3-methyl analogues of enone **4**, have been reported as unreactive toward the lumiketone rearrangement for reasons not at all clear at the present time,[8] there are two properties of **3** which appear to be unique in cyclohexenone photochemistry. One is that photoreduction of **3** at the C=C bond, strongly indicative of a reactive π,π^* triplet state,[3c,13,14,24,25] occurs even in *t*-BuOH and acetone, which are known to be unreactive as H donors toward n,π^* ketone triplets.[26] Thus, photorearrangement of **3** is slower than H abstraction even under conditions where the latter is expected to be unfavorable, contrary to the behavior of "normal" cyclic enones.[3,4,7,8,14] Secondly enone **3** exhibits fluorescence in fluid solution at room temperature, the first observation of such emission from a cyclohexenone.[27]

The fluorescence of enone **3** at room temperature in cyclohexane, methanol, and acetonitrile has a maximum at 385 nm; the excitation spectrum coincided with the UV absorption of **3**.[28] The fluorescence lifetime as determined by single photon counting was 0.26 ns. The emission was not quenched by CHD at concentrations sufficient to obliterate all photochemical reactivity. Loutfy and Morris[29] previously reported fluorescence from bicyclo[3.3.0]octenone **10**, attributed to an unusually large ${}^1n,\pi^*-{}^3\pi,\pi^*$ energy gap which inhibits intersystem crossing. We ascribe the observation of fluorescence of **3** to structural rigidity around the C=C bond, which inhibits rapid radiationless decay to a distorted geometry by twisting around the C=C bond, a decay process which can operate in unconstrained cyclohexenones. Thus, this suggests that unconstrained cyclohexenones may undergo intersystem crossing preferentially in nonplanar rather than planar geometries, contrary to usual assumptions.

We propose that the photochemical and photophysical properties of **3** are most readily understood in terms of the structural rigidity of **3** compared with that of other cyclohexenones studied to date. However, the surprisingly rapid nonproductive decay of the lowest triplet state of **3** needs to be explained, as well as the reason for the lack of reactivity toward rearrangement of some cyclohexenones[8] which appear to be unconstrained with respect to twisting around the C=C bond. These problems, as well as detailed studies of other constrained enones, are now under investigation in our laboratory.

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Electron-Beam-Induced Wolff Rearrangement

Sir:

The Wolff rearrangement[1] has attracted much interest both academically[2,3] and industrially.[4-6] For the most part this is due to the high reactivity of α-diazo ketones and the relative ease with which products may be chemically or spectroscopically analyzed. Mechanistic studies for electron-beam exposure

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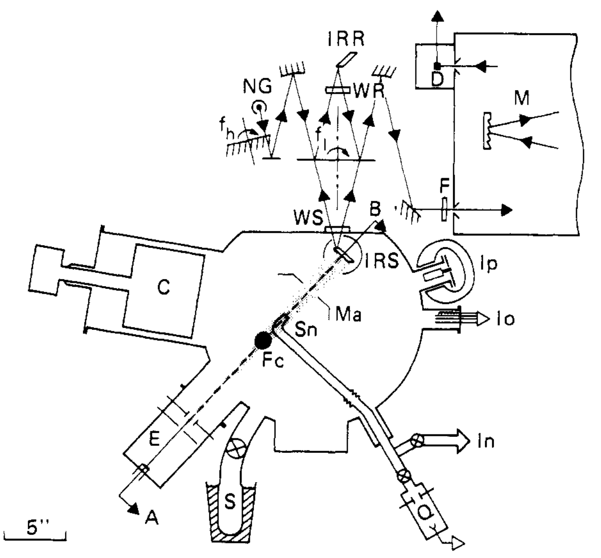


Figure 1. A schematic drawing of the apparatus for studying electron-beam-induced chemistry of organic thin films. System description: NG = Nernst glower; f_h = high frequency chopper; f_l = low frequency butterfly mirror; WR = window reference; WS = window sample; IRR = internal reflectance element reference; IRS = internal reflectance element sample; F = order sorting filter; M = monochromator; C = cryopump; D = detector; E = electron beam gun; S = sorption pump; Q = quadrupole mass spectrometer; In = inlet for gas mixture; Io = ionization gauge; Ip = ion pump; Sn = spray nozzle (for gas deposition); Fc = Faraday cup; Ma = mask.

of α-diazo ketones in the condensed phase are almost completely nonexistent in spite of the vast industrial importance of these compounds[4-6] and the intriguing questions concerning the fate of the Wolff rearrangement upon electron impact in the solid state. The reason why mechanistic studies are so scarce, in particular those involving the identification of intermediates, becomes quite obvious when one considers the very low penetration depth for electrons in the solid state[7] (≈ 4 μ for 30-keV electrons). As a consequence of this, chemical and spectroscopic analysis of the intermediates needed to establish a reaction mechanism induced by the electron beam in thin films becomes very laborious. However, since electron-beam exposure of organic solids is such a novel way of studying organic reactions and reactive intermediates, we have constructed an apparatus to investigate electron-beam-induced chemistry in the solid state.[8]

A schematic drawing of the experimental apparatus is shown in Figure 1. In essence, a thin film of the sample coated on one side of a CdTe total internal reflectance element is exposed to electrons by an electron-beam gun capable of operating at accelerating voltages up to 30 kV. The sample temperature may be varied from 8 to 400 K while under ultrahigh vacuum ($\sim 10^{-10}$ mmHg). The progress of the electron-beam irradiation is followed by total internal reflectance (TIR) spectroscopy.[9] This latter technique is especially important because the infrared spectrum of the thin film sample (<1 μ) can only be observed by multiple total internal reflections of the infrared light through the film. The ultrahigh vacuum requirement is also crucial because at higher pressures impurities such as water hydrocarbons, etc., are rapidly cryopumped on the TIR element and are easily detected owing to the long path length of the infrared light in the element.

The TIR infrared spectrum of the α-diazo ketone I recorded on this apparatus is shown in Figure 2 (solid trace). The infrared spectrum recorded after exposure to 6-keV electrons (dose = 1×10^{-5} C/cm^2) at 8 K is also shown in Figure 2 (dashed trace).

The spectrum of I has been transformed into the spectrum of the ketene II. The ketene II is easily generated photochemically and its infrared spectrum was thoroughly studied in other reports.[6,10] It was also photochemically generated in this experimental apparatus in order to demonstrate convincingly that the ketene II was formed by the electron-beam exposure. The infrared spectrum of ketene II generated photochemically is identical with that shown by the dashed trace in Figure 2.

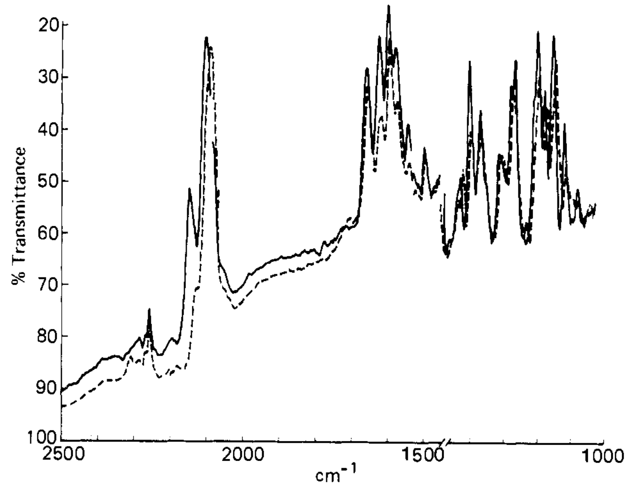
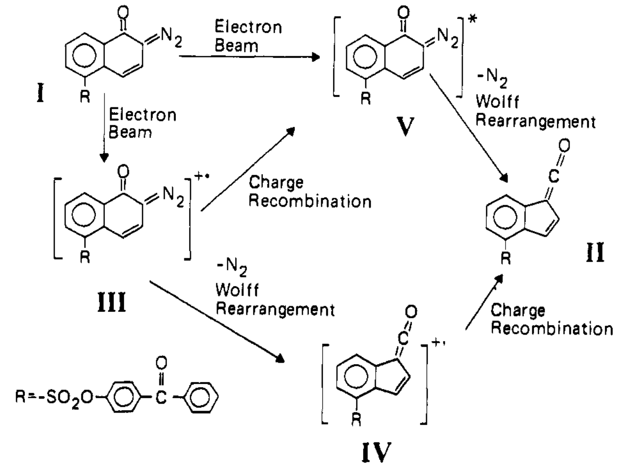


Figure 2. The infrared spectrum of a thin film (0.1 μ) of α-diazo ketone I (—). The infrared spectrum of the α-diazo ketone I after exposure to a 6-keV electron beam (dose = 10^{-5} C/cm^2) is shown as the broken trace (- -). All spectra were recorded and exposures performed at 8 K. The system pressure was $\approx 9 \times 10^{-10}$ mmHg.

It is interesting to speculate on the mechanism by which the ketene II was formed. Several reasonable possibilities are summarized in Scheme I. Mass spectroscopic[11-13] studies for electron impact on α-diazo ketones in the gas phase have indicated that a Wolff rearrangement occurs after ionization of the α-diazo ketone. Presumably, the rearrangement initiates on the potential surface of the radical cation of the α-diazo ketone. In a similar fashion it is conceivable that in the solid-state ionization of I to III, followed by rearrangement to IV and a charge recombination, could take place to ultimately form ketene II. It is also conceivable that the cation III could undergo charge recombination and form an excited state of the α-diazo ketone V which in turn eliminates nitrogen to form ketene II. Ion-pair formation and/or charge recombination are not necessary for the interconversion of I to II. Electron energy loss spectra[14] on thin films reveal that high-energy (kiloelectronvolt) electrons may directly excite optically observed electronic states and so the same electronic states involved in the photochemical generation of the ketene II may

Scheme I



be directly excited by the electron beam. Which of these mechanisms is the most important route for the electron-beam-induced Wolff rearrangement cannot be determined as yet. Further experiments are in progress in order to investigate this aspect of the problem.

In summary, an experimental apparatus has been constructed to study reactive intermediates induced by high- and low-energy electron beams. With this apparatus we have observed an electron-beam-induced Wolff rearrangement of an α-diazo ketone in the solid state.

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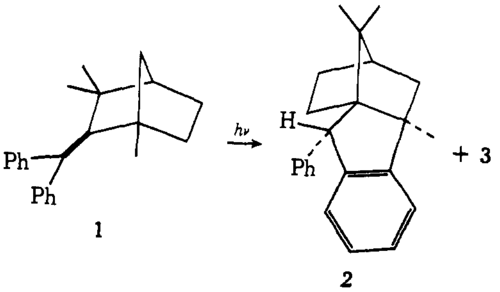
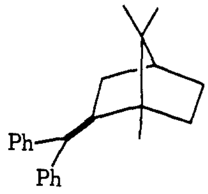
Photochemical Wagner-Meerwein Rearrangement of 2-Diphenylmethylenefenchane[1]

Sir:

Our interest in the photochemical reactions of β-substituted styrene and 1,1-diphenylethylene derivatives and in the possibility of observing reactions from twisted zwitterionic excited states[2] led us to a study of the photochemistry of the overcrowded olefin 2-diphenylmethylenefenchane (**1**).[3] We report that **1** undergoes a photochemical singlet-state Wagner-Meerwein rearrangement, a process which in ground-state chemistry is characteristic of a species having an electron-deficient carbon, and suggest the intermediacy of a twisted excited state of **1**.



1 **2**



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The photolysis[4] of **1** in methanol solvent under nitrogen proceeded slowly but cleanly to give two photoproducts, **2** and **3**, in 61 and 23% yields, respectively, at 23% conversion of **1**. Tedious chromatography (10% $AgNO_3$ on alumina, ether-hexane elution) of a photolysis mixture carried to higher conversion afforded pure samples of **2**, mp 119-120.5 °C, and **3** (oil). The 60-MHz NMR spectrum of the major photoproduct **2** showed three methyl singlets at δ 0.39, 1.10, and 1.15, multiplets at 1.20-2.00 (5 H), 2.17-2.60 (1 H), and 6.85-7.50 (9 H), and a 1 H singlet at 4.05. The spectrum of the minor product **3** was somewhat similar: methyl singlets at δ 0.13, 0.50, and 1.20, multiplets at 0.20-2.60 and 6.95-7.50, and, significantly, a singlet at 4.30.

The structure of photoproduct **2** has been established by single-crystal X-ray crystallographic analysis.[5] Crystal data: $C_{23}H_{26}$, orthorhombic, space group $P2_12_12_1$-D_2^4 (No. 19),[6] with $a = 9.138$ (4), $b = 11.355$ (4), $c = 16.794$ (13) Å; and $Z = 4$. A total of 1168 independent reflections having $2\theta_{\mathrm{Mo}\ K\bar{\alpha}} \leq 43°$ was collected on an Enraf-Nonius CAD4 automated diffractometer using the θ-2θ-scan mode and graphite monochromated Mo radiation. Initial fractional coordinates for the 23 crystallographically independent nonhydrogen atoms were obtained by direct methods (MULTAN). Anisotropic full-matrix least-squares refinement of the structural parameters for these 23 atoms and a scale factor has led to a conventional unweighted residual[7] $R = 0.088$ for the 900 reflections having $I \geq 2\sigma_I$.

Comparison of the NMR spectra of **2** and **3** and consideration of reaction mechanisms (vide infra) suggest that the latter compound is a diastereomer of **2**; however, this has not been rigorously established. Preliminary results indicate that 2-diphenylmethylenecamphane (**4**)[2] behaves similarly to **1**.[8]

The formation of **2** and **3** takes place in cyclohexane and acetonitrile as well as methanol. Sensitization of **1** with benzophenone in *tert*-butyl alcohol (uranium glass filter) for a prolonged period afforded no detectable rearrangement; **2** and **3** are therefore singlet derived. Quantum yield measurements[9] confirmed the qualitative observation that rearrangement of **1** is inefficient. In cyclohexane, $\phi_2 = 0.0013$ and $\phi_3 = 0.00066$, whereas in acetonitrile $\phi_2 = 0.00034$ and $\phi_3 = 0.00038$. The quantum yield values in acetonitrile are probably accurate to only ~25%.

A likely mechanism for conversion of **1** to **2** (and **3**) is shown in Scheme I. It is noted that the initial phase of the rearrangement is a $[\sigma + \pi]$ analogue[10,11] of the di-π-methane reaction.[12] The low quantum yield for the reaction of **1** is in accord with previous observations that such $[\sigma + \pi]$ rearrangements are inefficient and much less rapid than comparable reactions proceeding via initial $[\pi + \pi]$ interaction.[11,13]

A major point of interest is the structure of the reactive excited state of **1**, for a twisted, nonspectroscopic excited state is an attractive intermediate. Olefins, including styryl systems such as **1**, undergo facile rotation about the double bond to orthogonal geometries from their π,π^* singlet states.[14-19] Conversion into a twisted excited state ought to be particularly rapid with **1** in view of the substantial congestion about the double bond and the stabilization afforded the twisted species by the phenyl and alkyl substitution. Indeed, it is probable that the ground state of **1** is itself distorted from planarity.[20] We have been unable to detect fluorescence from **1** ($\phi_f < 0.0006$ in cyclohexane at room temperature by comparison with 1,1-diphenylethylene for which $\phi_f = 0.003$[21]), a finding consistent with the notion that **1** undergoes rapid excited-state twisting and that the spectroscopic singlet of **1** is very short lived.

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