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 $\alpha$-diazo ketone in the solid state.

**Acknowledgment.** The technical assistance of Mr. Fred Rodgers is gratefully appreciated.

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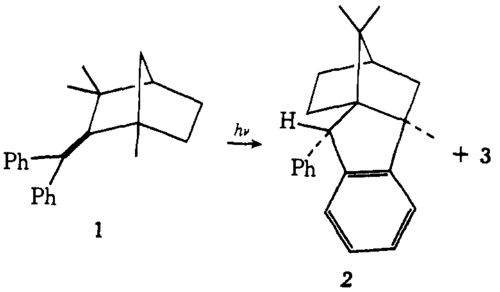
(15) Physikdepartment E13, TU München, D8046 Garching, West Germany.

**J. Pacansky,* H. Coufal**[15]
*IBM Research Laboratory, San Jose, California 95193*
*Received August 23, 1979*

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

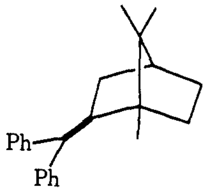
*Sir:*

Our interest in the photochemical reactions of $\beta$-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**



**4**

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 $\delta$ 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 $\delta$ 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 $2\theta_{\text{Mo K}\bar{\alpha}} \leq 43°$ was collected on an Enraf-Nonius CAD4 automated diffractometer using the $\theta$-$2\theta$-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-$\pi$-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 $\pi,\pi^*$ 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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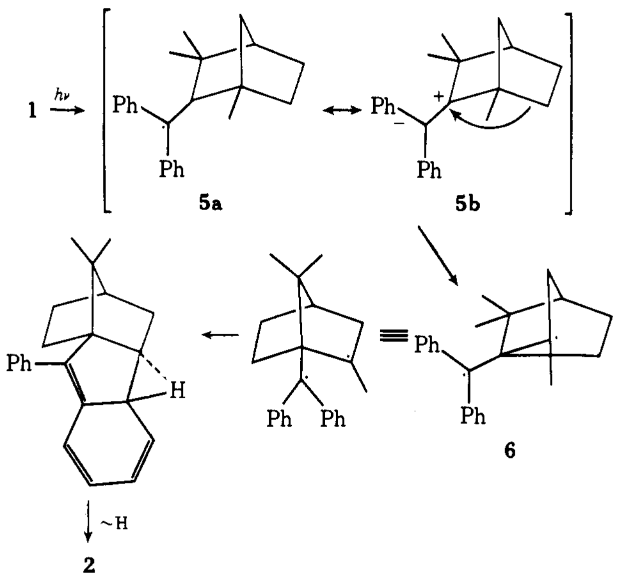
Scheme I



With the data at hand one cannot tell for certain whether **1** rearranges in competition with or subsequent to twisting. The nature of the rearrangement is compatible with the latter. Theory indicates that twisted olefin excited singlet states are highly polarizable and that under appropriate circumstances such as asymmetric substitution substantial net polarization can occur.[2] It has been suggested that orthogonal zwitterionic states are involved in certain diene and triene photochemical reactions and also play a major role in the photochemistry of vision.[2b,c,22,23] In the present reaction, the fact that alkyl migration to C-2 of **1** occurs strongly suggests that this carbon has become electron deficient on excitation and that ionic resonance structure **5b** is a major contributor to the reactive excited state.[24] Thus our observations point toward the intermediacy of a twisted, polar excited state in the rearrangement of **1**. It has previously been suggested that twisted singlet states mediate the photochemical olefin → carbene transformations of certain β-substituted 1,1-diphenylethylenes.[26]

**Acknowledgment** is made to the National Science Foundation for financial support.

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(5) While the absolute configuration of the product **2** is not provided by the X-ray data, the enantiomer of **2** shown is that derived from **1** (obtained from D-fenchone[3]) via the mechanism in Scheme I.
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(8) Irradiation of a methanol solution of **4** to 94% conversion afforded three products in yields of ~11, 11, and 6%. The NMR spectra of the two major products showed inter alia singlets at δ 4.00 and 4.45, suggesting structures analogous to **2** and **3**. We have been unable to obtain the minor product in a quantity sufficient for characterization.
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**Stephen S. Hixson,* Roberta O. Day**
**Lothar A. Franke, V. Ramachandra Rao**
*Chemistry Department, University of Massachusetts*
*Amherst, Massachusetts 01003*
*Received July 9, 1979*

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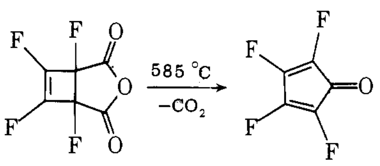
## Perfluorocyclopentadienone

*Sir:*

We report here the synthesis and some chemistry of the title compound. Unlike cyclopentadienone itself, which has been observed only at low temperatures in matrix isolation,[1] the perfluoro derivative can be conveniently manipulated at room temperature as an orange vapor.[2,4]

Sublimation in vacuo through a Vycor tube heated to 585 °C transforms tetrafluorocyclobutenedicarboxylic anhydride[5] (**2**) into dienone **1** in a remarkably clean fragmentation process.



**2** **1**

Trapped at −196 °C, the dienone can be preserved neat or in solution at low temperatures or sublimed on warming into a gas storage bulb to be kept for many hours at low pressure. At room temperature it dimerizes very rapidly in the liquid phase.

The mass spectrum of **1** shows a parent peak at *m/e* 152 and a very prominent peak at *m/e* 124 ($M^+$ − 28), probably the tetrafluorocyclobutadiene radical cation. Its IR spectrum has been measured in the vapor phase at room temperature, but resolution is much better in an argon matrix at 12 K. The double-bond stretching region is reproduced in Figure 1. Since fluorinated double bonds have stretching frequencies in the ketone region, all three bands probably represent strongly coupled vibrations.[6] Comprising multiplets of equal area at 136.86 and 173.41 ppm,[7] the $^{19}$F NMR spectrum ($CH_2Cl_2$, −90 °C) is of the AA′XX′ type, with intraset $|J|$ values of 11.2 and 27.4 Hz and interset $J$ values of ±11.8 and ∓17.9 Hz (Figure 2). The electronic spectrum of the vapor at room temperature reveals an intense maximum at 198.5 and a broad, weak maximum at 390 nm [cf. 3-*tert*-butylcyclopentadienone, $\lambda_{max}^{isooctane}$ 200 nm (log ε 4.71) and 380 (>1.9)].[8]

Dimerization of tetrafluorocyclopentadienone yields a single isomer whether the reaction occurs in the vapor phase, neat liquid or solvents ranging widely in polarity. Remarkably, this