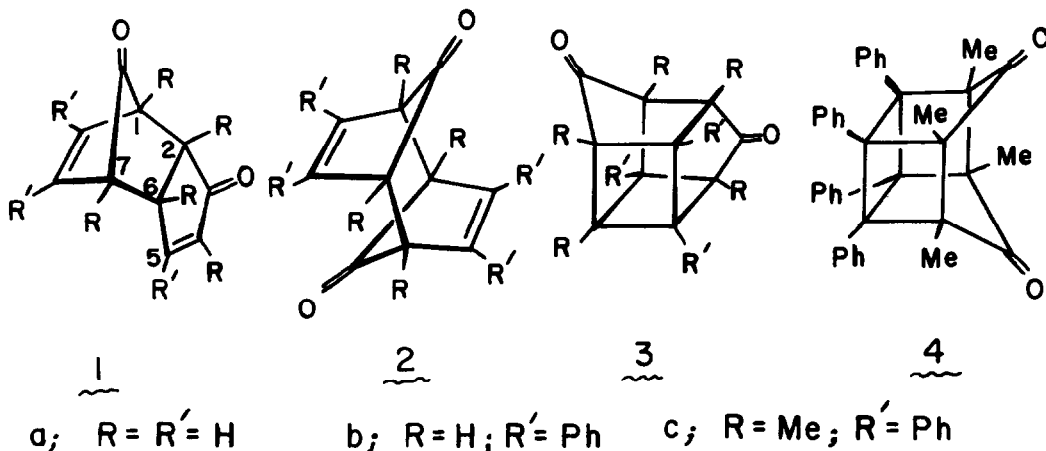


PHOTOCHEMISTRY OF CYCLOPENTADIENONE DIMERS

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The photochemistry of several cyclopentadienone dimers, 1, has been reported recently. The excited singlet states of 1a and 1b undergo [1,3] sigmatropic shifts to form 2a and 2b, while the triplet state of 1a forms the [2+2] cage isomer 3a.^{1,2} Recently, Fuchs reported

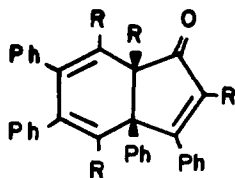


that the photochemistry of 1c is anomalous since 4 along with traces of 3c are produced upon photolysis of 1c. Fuchs concluded that the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone 1c has the exo configuration², contradicting an earlier conclusion of Warrenner and co-workers.³

Since 1c dissociates in solution, while 1a and 1b are thermally stable,⁴ we chose to investigate more closely the photochemistry of 1b and 1c. In the course of these investigations, we have discovered that the photochemistry of cyclopentadienone dimers is extremely sensitive

to substituents, multiplicity, physical state, and wavelength of irradiation. In addition, the endo configuration of $\underline{1c}$ has been proven.

Photolysis of $\underline{1c}$ (acetonitrile solution, 10° , Pyrex filter, RUL-3500Å lamps) produced the exceedingly insoluble cage isomer $\underline{4}$, mp 273° d (lit.² 272°) in 70% yield, in agreement with Fuchs' report.² However, sensitized photolysis of $\underline{1c}$ (10° , quartz, RUL 2537Å, acetone absorbing ~70% of the light) resulted in formation of the "normal" cage isomer $\underline{3c}$,⁵ mp $321-323^\circ$. Direct irradiation of $\underline{1c}$ at short wavelengths (acetonitrile, 10° , quartz, RUL-2537Å) resulted exclusively in decarbonylation to form $\underline{5b}$, mp $166-168^\circ$ in 70% yield, identical in all respects to the product of thermal decarbonylation, isolated in 30% yield after heating $\underline{1c}$ at 220° ⁷.



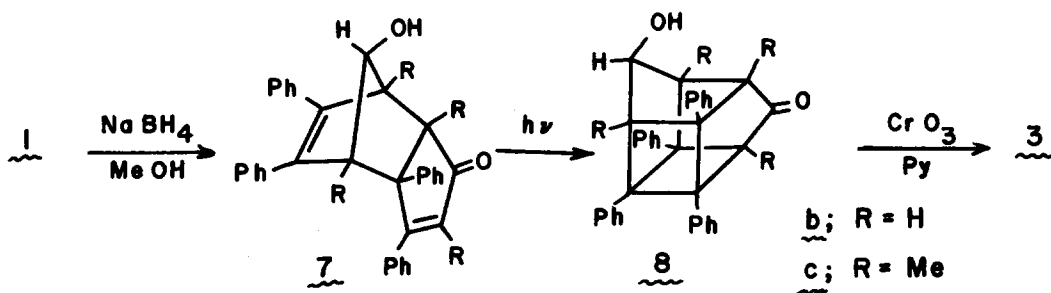
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a; R = H

b; R = Me

A similar wavelength dependence was noted with $\underline{1b}$. Irradiation of $\underline{1b}$ at long wavelengths (acetonitrile, 10° , Pyrex, RUL-3500Å) resulted in the formation of a 30% yield of the [1,3] shift product, $\underline{2b}$, mp 252° (lit.² 257°) while direct photolysis of $\underline{1b}$ at short wavelengths (acetonitrile 10° , quartz, RUL-2537Å) results exclusively in decarbonylation. However, in this case, $\underline{5b}$ is not isolated but is believed to undergo rapid transformation to an isomer $\underline{6}$, mp $188-191^\circ$, isolated in 60% yield, whose structure is under investigation.⁸ No new photoproduct was observed on attempted sensitization (acetone, absorbing ~70% of the light).

Except for the formation of $\underline{4}$, a consistent pattern of reactivity emerges assuming all cyclopentadienone dimers have the endo configuration. Further support for the endo stereochemistry of $\underline{1c}$ was obtained as follows: Reduction of $\underline{1c}$ ($\text{NaBH}_4/\text{MeOH}$) gave the mono-alcohol $\underline{7c}$,⁵ mp $190-194^\circ$ [ir (KBr) 6.00μ ; nmr (CDCl_3) Me singlets at δ 0.98, 1.24, 1.88, and 2.20]. Both direct (acetonitrile, 10° , Pyrex, RUL-3500Å) and sensitized (acetone, 10° , quartz, RUL-2537Å) photolysis of $\underline{7c}$ resulted in formation of caged isomer $\underline{8c}$,⁵ mp $301-302^\circ$ [ir (CCl_4) 2.76, 5.71μ ; nmr (CDCl_3) Me singlets at δ 0.53, 0.70, 1.63, and 1.88; uv, $\lambda_{\text{max}}^{\text{MeOH}}$ 223 nm (ϵ 2.3×10^4)] as the only product. Chromic anhydride-pyridine oxidation of $\underline{8c}$ gave $\underline{3c}$. Parallel results were obtained beginning with $\underline{1b}$. Since $\underline{7c}$ does not dissociate at less than 100° , the configuration of $\underline{7c}$ (endo) must be the same as that of $\underline{1c}$.



Apparently, the lowest enone singlet of the cyclopentadienone dimers lead to [1,3] shifts in $\underline{1a}$ and $\underline{1b}$, while in $\underline{1c}$ the rearrangement may be retarded by torsional strain which would develop between the 1- and 2-methyls in the [1,3] shift mid-point. The triplet states undergo [2+2] intramolecular cycloadditions from $\underline{1a}$, $\underline{1c}$ and the derivatives $\underline{7b}$ and $\underline{7c}$. An upper excited state in $\underline{1b}$ and $\underline{1c}$ (apparently not in $\underline{1a}$) decarbonylates. This state may be populated in a dissociative level⁹ or may undergo decarbonylation faster than intramolecular energy transfer.¹⁰

The mechanism for formation of $\underline{4}$ remains an intriguing puzzle. Since $\underline{1c}$ has the endo configuration, dissociation must occur at some stage in the mechanism for formation of $\underline{4}$. The solid-state photolysis of $\underline{1c}$ is consistent with this conclusion.¹¹ Thus, irradiation (RUL-3500Å) of crystalline $\underline{1c}$ deposited on the walls of a Pyrex tube resulted in formation of $\underline{3c}$ in 43% yield along with $\underline{4}$ in 15% yield. In the crystalline state, dissociation of $\underline{1c}$ may be physically hindered, such that either intersystem crossing to the triplet of $\underline{1c}$ occurs in competition with dissociation, or the singlet of $\underline{1c}$ forms the cage adduct $\underline{3c}$ at a rate competitive with the rate of formation of $\underline{4}$. While thermal dissociation of $\underline{1c}$ prior to photochemical rearrangement to $\underline{4}$ may be necessary, an unprecedented alternative would be photodissociation of the $\underline{1c}$ singlet to form an excited cyclopentadienone and ground state cyclopentadienone, either in a solvent cage or as an exciplex. Collapse of this pair or exciplex in an excited state allowed [4+4] or [2+2] fashion, followed by photochemical intramolecular [2+2] cycloaddition would form $\underline{4}$.

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- (1) E. Bagglioni, E.G. Herzog, S. Iwasaki, R. Schorta and K. Schaffner, Helv. Chim. Acta, 50, 297 (1967).
- (2) B. Fuchs, J. Amer. Chem. Soc., 92, 2544 (1971). We thank Dr. Fuchs for a copy of his manuscript prior to publication.
- (3) C.M. Anderson, I.W. McCay and R.N. Warrener, Tetrahedron Lett., 2735 (1970).
- (4) M.A. Ogliaruso, M. Romanelli and E.S. Becker, Chem. Reviews, 65, 261 (1965).
- (5) All new compounds gave elemental and spectral data in accord with the assigned structures, with the exception of 6, whose structure has not yet been proven.
- (6) Although the thermal decarbonylation product, 5b, has been reported, no mp or spectral data have been previously reported: ir (CCl₄) 5.87 μ ; nmr (CDCl₃) δ 0.73 (s, 3H), 0.92 (s, 3H), 1.51 (s, 3H), 1.88 (s, 3H), 6.5-7.5 (20H); uv (EtOH) 240 (ϵ 5.7 \times 10⁴); mass spectrum (70 eV) m/e 492 (M⁺).
- (7) C.F.H. Allen and E.W. Spangel, J. Amer. Chem. Soc., 55, 3773 (1933); F.W. Gray, J. Chem. Soc., 95, 2132 (1909).
- (8) Thermal decarbonylation of 1b to 5b⁷ followed by photolysis gives 6, mass spectrum (70eV) m/e 436 (M⁺).
- (9) For a discussion of other wavelength dependent photochemistry, see E.F. Ullman, Accounts Chem. Res., 1, 353 (1968).
- (10) For a discussion of intramolecular energy transfer, see A.A. Lamola, J. Amer. Chem. Soc., 91, 4786 (1969).
- (11) While we have proven that dissociation of 1c must occur at some stage in the mechanism, other experiments designed to obtain mechanistic evidence have proven fruitless so far. For example, the monomer 2,5-diethyl-3,4-diphenylcyclopentadienone does not undergo photodimerization to an analog of 4.