$$2RuL_3^+ + 2H^+ \xrightarrow{PtO_2} 2RuL_3^{2+} + H_2 \qquad (5)$$

$$23 + 2H^+ \xrightarrow{PtO_2} 2CH_3CH{=}NEt_2^+ + H_2 \qquad (6)$$

$$RuL_3^+ + PtO_2 \rightarrow RuL_3^{2+} + \text{“}PtO_2^-\text{”} \qquad (7)$$

The results reported here appear somewhat related to those obtained by Lehn and Sauvage[6] and by Kalyanasundarum et al.[8] and others,[9,10] where irradiation of metal complexes in the presence of platinum catalyst systems and other reagents also leads to hydrogen production. However, the present results involve a much simpler system and a high quantum efficiency. It is particularly noteworthy that in this case the primary photoproduct RuL_3^+ is directly and efficiently coupled to water reduction. Like the other systems, the present results involve water reduction at the expense of an external reductant, in this case triethylamine. Thermochemical data[23] indicate that the overall reaction (eq 8) is moderately endothermic ($\Delta H \simeq$ 14 kcal/mol). We are currently extending our studies using other metal complexes in which ligand modification affords both proton binding sites and a more favorable reduction potential, so that milder reducing agents can be used.

$$Et_3N + H_2O \xrightarrow[RuL_3^{2+}\ \text{visible light}]{} Et_2NH + CH_3CHO + H_2 \qquad (8)$$

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(19) Both a 100-W (General Electric H100PSP44-4) lamp filtered through 9 cm of H_2O and a Corning 3-74 filter and a 1000-W mercury-xenon (Hanovia 977-B0010) lamp with the 436-nm line selected by a Bausch and Lomb (33-86-79) monochromator were used in these experiments. Actinometry for the latter lamp was by Reinecke's salt and ferrioxalate. Analysis for hydrogen was carried out using a gas chromatograph with a 7-ft alumina column cooled to −75 °C and by mass spectrometry. Quantitative analysis was by the former; a calibration curve between the injected amount of H_2 gas and the signal response was linear over the range of samples used. In a typical experiment, 4 mL of solution was irradiated with a volume of 1 mL above the solution. The irradiation time was 45-60 min, and the hydrogen produced was 5×10^{-5} mol in the 1-mL volume.

(20) Uncorrected for light absorption by the suspended catalyst; the corrected quantum yields are as high as 0.44 for **2** and 0.53 for **1** before depletion takes place.

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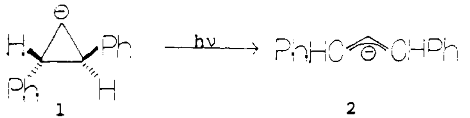
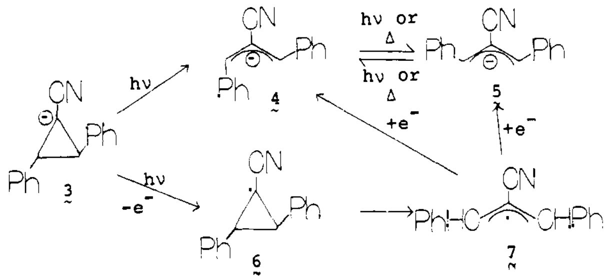
Orbital Topology in a Photochemical Carbanionic Ring Opening

Sir:

Although orbital topological control in thermal pericyclic reactions of carbanions has been amply demonstrated,[1] its importance in photochemical carbanionic ring openings remains uncertain.[2] The symmetry-predicted disrotatory excited-state opening of trans-2,3-disubstituted cyclopropyl to allyl anions, e.g., **1** to **2**,[3] should potentially provide convenient systems for further study since the expected product should convert, by analogy to the 1,3-diphenylpropenyl anion **2**, only slowly into its geometric isomer if the photolysis is conducted at sufficiently low temperatures.[4-6]



Thus, the production of a nonequimolar mixture of *cis*- and *trans*-α-benzylcinnamonitrile upon low-temperature proton quench of the photochemically ring-opened product derived from **3** has several possible interpretations. Among these are (1) a symmetry-controlled disrotatory opening to **4**, the expected *E,Z* isomer, followed by thermal geometric equilibration, possibly during protonation;[5] (2) a photoinduced cis-trans isomerization (**4** ⇌ **5**), a known process for **2**;[6] (3) a photoinduced electron ejection from **3** to form the corresponding radical **6** which could open[7,8] to the ultimately stereorandom[8] allyl radical **7** before recapturing an electron to form a mixture of **4** and **5**; or (4) an absence of orbital symmetry direction of the ring opening. A reexamination of this reaction originally studied by Newcomb and Ford[3] suggests that, in the absence of complicating secondary reactions, the disrotatory mode predicted by orbital symmetry can be observed, possibly by two primary photochemical pathways.



Upon irradiation with a Pyrex-filtered 450-W medium-pressure mercury lamp, a solution of **3**[3] (5×10^{-3} M) in THF-d_8 (generated by treating *cis,trans*-2,3-diphenylcyclopropanecarbonitrile with lithium diisopropylamide) at −70 °C became bright red, indicating the formation of **4** and/or

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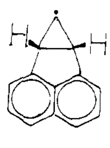
5. Aliquots were periodically removed for analysis by ^{1}H NMR and, after protonation, by GLC (5 ft × $^1/_8$ in., 20% SE-30 on 60/80 Chromosorb P). The formation of **4** (δ 5.4, 4.6 ppm) could easily be distinguished from that of **5** (δ 4.9 ppm) and quenching at −70 °C gave two product peaks by GLC. With the proof that **4** gave a nearly equimolar mixture of *cis*- and *trans*-α-benzylcinnamonitrile and with the reasonable assumption that **5** should give only the trans isomer, the relative abundance of the two GLC peaks implied the existence of a **4–5** mixture before quench which was identical with that obtained by NMR integration of the anion signals. At 50% conversion of **3**, a 3:1 mixture of **4–5** was obtained. Upon modifying these photolysis conditions by adding a Corning 7-54 visible light filter ($300 < \lambda_{ex} < 420$ nm), the photoconversion proceeded somewhat more slowly but with greater stereocontrol. Subsequent control experiments demonstrated that thermal opening of **3** does not occur at −70 °C, that thermal reversion of **5** to **4** was slow at −70 °C on the experimental time scale (~$^1/_2$ h), and that the rapid photointerconversion of **4** and **5** which occurred with a Pyrex-filtered mercury arc was significantly slowed by the visible light filter. The fraction of **4** (**4**/(**4** + **5**)) decreased as the reaction proceeded but extrapolation to 0% conversion gave >95% production of **4**.

This preference for disrotatory opening can be explained either as a concerted photochemical opening of a cyclopropyl anion, as a concerted thermal opening of a cyclopropyl radical formed by photoinduced electron ejection, or as a thermodynamically controlled pathway operating independently of orbital topological constraint. The first possibility is in accord with simple application of the Woodward-Hoffmann rules. The second possibility is more uncertain. Theory predicts that opening of the cyclopropyl radical should proceed more slowly than the openings of either the cyclopropyl anion or cation[10] and most experimental studies of the stereochemical mode have been hampered by apparently lower barriers for geometrical isomerism in allylic radicals than for cyclopropyl ring opening[8] (and by the mode of preparation of the cyclopropyl radical, usually by pyrolysis of a peroxide or azine precursor). Early extended Hückel calculations[9] predicted a conrotatory mode for the opening of the unsubstituted cyclopropyl radical, but more recent semiempirical and ab initio theoretical considerations have agreed that the disrotary mode should be favored.[10] Although the existence of barriers to thermal ring opening of cyclopropyl radicals has theoretical and experimental support, the barrier to opening in **6** should be reduced by the extended conjugation in **7**.[7,8] Radical **8**, for example, is known to open even at −90 °C by a disrotary mode.[11]



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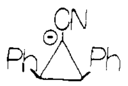

9

The importance of the electron ejection pathway could be evaluated by conducting the photolysis of **3** in the presence of *cis*-stilbene. If the flash of a N_2 laser was used as excitation source in such a mixture, a transient was observed at ~490 nm, consistent with the production of the *cis*-stilbene anion radical.[12] Upon repetition of the experiment under steady-state irradiation where light absorption by stilbene is minimized, *cis*-stilbene was slowly converted into the trans isomer. The rate of the olefin isomerization was at least 10 times faster than its rate in the absence of light. Such observations are suggestive[13] of photoinduced electron transfer from **1** to an acceptor (stilbene).

Whether this primary photochemical electron ejection can occur in the absence of a good acceptor is more difficult to establish. Such a pathway could be ruled out if it could be shown that the product of such a transfer (**6**) undergoes alternate reactions (e.g., H abstraction or dimerization) faster than ring opening under the reaction conditions of the photolysis. This possibility was examined by oxidizing **3** with anhydrous $CdCl_2$[14,15] at −70 °C. A complex mixture which was produced contained dimeric product (10–20%), a portion of which is ring opened.[18] The detection of such ring-opened product makes difficult the exclusion of the radical pathway, at least as a minor route to **4**, but the cleanness of the photochemical conversion of **3** into **4** + **5** (>90% mass balance) provides a sharp contrast to the diversity of products obtained in the oxidative reaction of **3**.

Analogous low-temperature photolysis of **9**, the 1-cyano-*cis*-2,3-diphenylcyclopropyl anion, proceeds by a nearly completely different reaction course in which ring opening represents a minor pathway.[19] If a stereorandom pathway to the more stable isomer **4** directs the ring opening of **3**, then **9** (which is less stable than **3**) might be expected to open to **4** even more rapidly than does **3**. Since **9** resists ring opening and disappears more slowly than **3**, other factors must be at play.

Our results clearly establish that the photochemical ring opening of **3** is stereochemically nonrandom. The observed disrotatory mode of the opening can be explained by a photochemical cyclopropyl anion opening and/or by a thermal cyclopropyl radical opening. Efforts are continuing in our laboratory to determine those factors which can direct an anionic excited state toward pericyclic reaction or toward electron transfer and to characterize alternate reaction pathways adopted (e.g., by **9**) when transition states favored by orbital topology become disfavored by secondary thermodynamic restraints.

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(13) The possibilities that the isomerization occurs through minor light leakage to directly excite stilbene or by energy transfer from an anion excited state have not been definitively excluded. The photolysis mixture derived from **3** is more complex when the reaction is conducted in the presence of stilbene. Although the yield of ring-opened hydrocarbons is greatly reduced, GLC analysis of the quenched products indicates that formation of **4** is preferred to that of **5**, but by smaller fraction (~2:1) than is observed in the photolysis in the absence of stilbene.

(14) Electrochemical oxidation of **1** (1 mM in NH_3 with KI as inert electrolyte)

occurred at −1.7 eV vs. Ag quasi-reference electrode, implying that oxidation by Cd(II) should occur readily. The possibility of ring opening by further photoinduced reduction of **3** to a radical dianion is unlikely in view of this potential. Although Newcomb et al. have shown that opening by a radical anion route occurs rapidly if a neutral aryl cyclopropane is treated with strong base,[16] this route to ring-opened product appears to be unimportant if **3** is generated with lithium diisopropylamide. **3** can be essentially quantitatively methylated if the solution of **3** in THF is quenched by methyl iodide.[17]

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(18) A ^{1}H NMR spectrum of the dimeric fraction (*m/e* 438) exhibited signals in the vinylic region.

(19) Upon photoexcitation, **9** reacts at least three times more slowly than does **3**, despite the similarity of their absorption spectra. The absence of red color in the photolysis mixture indicates that its disappearance proceeds through intermediates different from **4** and/or **5**.

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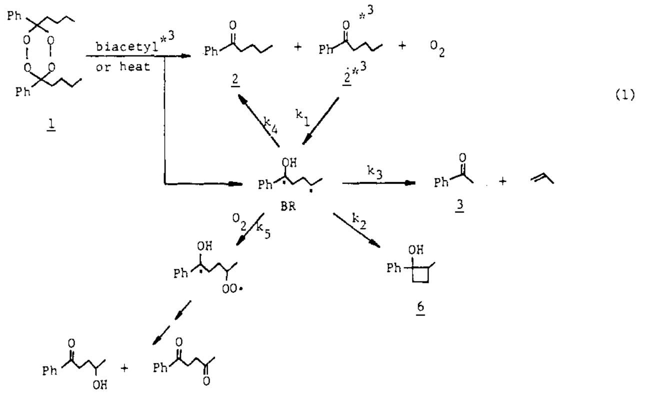
Formation of the Norrish Type II Products from the Biacetyl-Sensitized Photolysis of Valerophenone Diperoxide

Sir:

In connection with the chemistry of high-energy-content molecules which contain an intramolecular probe for excitation,[2] we have recently reported[1b] that the triplet excited state of valerophenone (**2**) may be formed by the thermal and biacetyl-sensitized decomposition of valerophenone diperoxide (**1**) (eq 1). We now report evidence that acetophenone (**3**), one of the Norrish type II products of **2**,[3] comes from a 1,4 biradical (BR) which is formed directly by the biacetyl-sensitized decomposition of **1** without going through triplet valerophenone.



The type II reaction of **2** in benzene is known to occur from the triplet n,π* excited state of **2** to produce exclusively the 1,4 biradical ($k_1 \sim 1.3 \times 10^8$ s^{-1}) which (a) disproportionates back to **2** ($k_4 \sim 1.8 \times 10^7$ s^{-1}), (b) fragments to **3** and propylene ($k_3 \sim 1 \times 10^7$ s^{-1}), or (c) closes to form 2-methyl-1-phenylcyclobutanol (**6**) ($k_2 \sim 0.2 \times 10^7$ s^{-1}).[3]

A solution of **1**[4] in benzene (~10^{-2} M) containing various concentrations of biacetyl as a sensitizer (0.01–2.3 M) was irradiated with light of >400-nm wavelength under bubbling nitrogen to give valerophenone (**2**), acetophenone (**3**), γ-hydroxyvalerophenone (**4**), 1-phenylpentane-1,4-dione (**5**), and biphenyl (Table I) in addition to a small yield of butyl benzoate (<5%).[5] In a separate experiment all of these products were isolated and identified by direct comparisons with authentic samples. Traces of phenyl valerate could occasionally be detected (<2%).

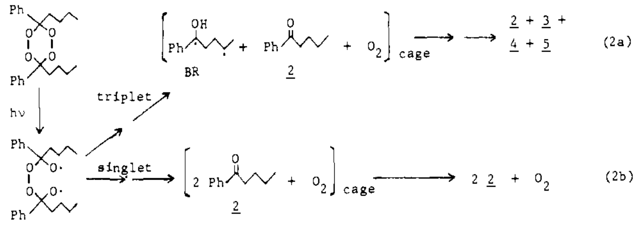
Table I. Biacetyl-Sensitized Photolysis of Valerophenone Diperoxide (**1**) in Benzene[a]

biacetyl, M	irradn time, h	products, %[b,c] **2**	**3**	**4**	**5**	Ph_2	recovd **1**, %[b]
0.010	18	15	9	6	11	25	83
0.034	10	23	15	5	17	31	82
0.225	10	27	24	5	10	19	74
0.46	11	29	33	8	13	10	76
1.15	8	20	27	9	8	3	76
2.30	8.5	12	22	7	7	2	75

[a] Irradiations were carried out with a 400-W high-pressure mercury lamp through a 10% sodium nitrite solution (>400 nm) at room temperature under bubbling nitrogen which was deoxygenated by passing through an alkaline pyrogallol solution. A control experiment was done in every case. [b] Estimated errors ±50%. [c] The yield of 2-methyl-1-phenylcyclobutanol (**6**) was negligibly small.[7]

It should be noted that the yield of **3** did not decrease or even increase with increasing concentration of biacetyl, indicating that triplet valerophenone is not a precursor of **3**. The biacetyl would have quenched any triplet valerophenone, since k_q(**2**^{*3} → biacetyl) ~ 1.5×10^9 M^{-1} s^{-1} in benzene.[6]

Our VPC showed that there was formed only a negligible amount of the other type II product (**6**).[7] However, we believe that **3** was formed via the 1,4 biradical, since **4** and **5** were produced simultaneously with **3**. The production of **4** and **5** can be rationalized by assuming that BR is trapped in a solvent cage with oxygen which may be formed together with BR from the decomposition of the peroxide **1** (eq 2a).[8] Recently Small and Scaiano[9] have shown that oxygen interacts with the 1,4 biradical with $k_5 \sim 8.4 \times 10^9$ M^{-1} s^{-1} in benzene. As was suggested by them,[9] we found that irradiation of **2** in benzene under bubbling oxygen, followed by treatment of the reaction mixture with triphenylphosphine, produced **4** (7%) and **5** (0.5%) along with **3** (83%) and **6** (9%).[10]



The intermediacy of the biradical in the biacetyl-sensitized photolysis of the peroxide **1** also seems corroborated by the effect of alcohol; the quantum yield of **3** from the sensitized photolysis of **1** in benzene increased with increasing concentration of added *tert*-butyl alcohol or 3-ethyl-3-pentanol, as is expected from Wagner's report.[11,12]

Biphenyl quenches biacetyl phosphorescence inefficiently with k_q(biacetyl^{*3} → biphenyl) ~ 3.2×10^3 M^{-1} s^{-1} in benzene[6] and quenches the type II reaction of **2** efficiently with k_q(**2**^{*3} → biphenyl) ~ 1.4×10^9 M^{-1} s^{-1} in benzene.[6] The formation of **3** from the biacetyl-sensitized photolysis of **1** in benzene (0.11 or 0.057 M biacetyl) was somewhat quenched by diphenyl (0.05–0.5 M), and the quenching data are totally explicable in terms of the quenching of triplet biacetyl,[13] not triplet valerophenone. It is now quite reasonable to conclude (1) that the decomposition of peroxide **1** is initiated by triplet biacetyl to result in the efficient formation of **3** without the

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