In conclusion, we draw attention to the fact that our (hydro)methylation method can, in favorable cases, produce any of the four possible arrangements of a methyl and a hydrogen adjacent to the original carbinol center. This is illustrated by considering the ketones derived from **7** and **8**, respectively: It is a consequence of their mode of formation that they both have an axial 4-methyl group. Equilibration via the ketone thus makes available the other two (equatorial) epimers. It follows that in systems related to **1**, **5**, and **6**, in which the unsaturated β-center is part of a ring junction, control of the ring junction stereochemistry[1a] can be achieved independently of that of the stereochemistry at the center adjacent to the hydroxyl group.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for financial support of this work.

Electron Transfer Photochemistry of Aromatic Imides and Phenylcyclopropane. Radical Anion-Radical Cation Cycloaddition

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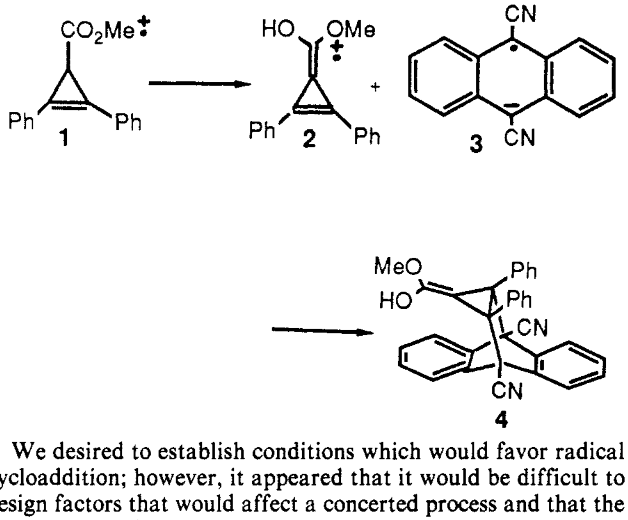
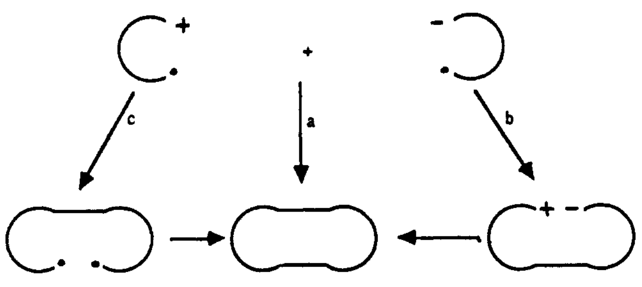
Received June 16, 1986

The most obvious reaction of a photochemical electron transfer generated radical anion–radical cation pair is cycloaddition which could occur concertedly (path a) or by the two-step processes outlined in Scheme I (paths b, c). However, there are no clear examples of this cycloaddition[1] presumably because competing processes such as reverse electron transfer and proton transfer from the radical cation to the radical anion[2] dominate the cycloaddition process. Perhaps the closest example of this reaction is the formation of **4** by the addition of the methyldiphenylcyclopropene carboxylate radical cation (**1**), after preliminary enolization (**2**), to the dicyanoanthracene radical anion (**3**).[3]



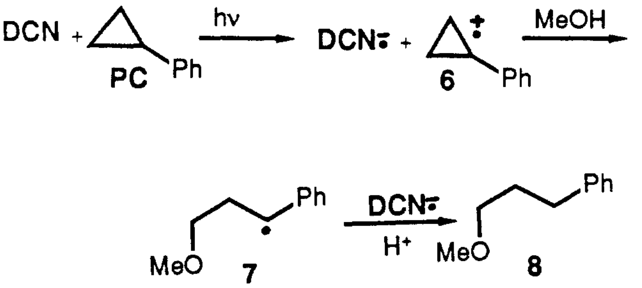
Scheme I



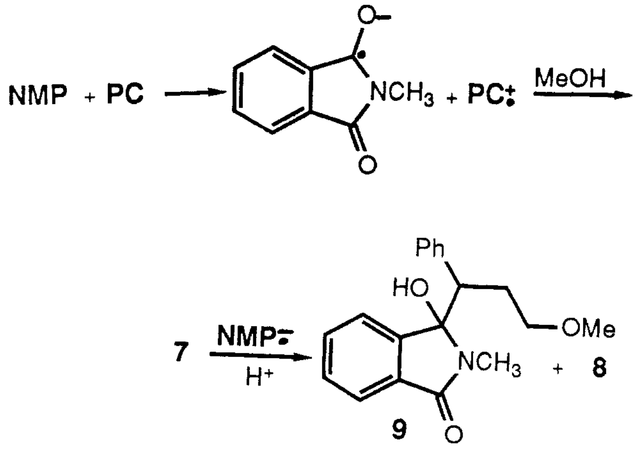
I

We desired to establish conditions which would favor radical cycloaddition; however, it appeared that it would be difficult to design factors that would affect a concerted process and that the process initiated by radical coupling to a zwitterion (path a) would probably result in intramolecular proton transfer as it has in other cases.[2d-f] However, nucleophilic addition of the radical anion to the radical cation (path c) would afford a biradical which should undergo the desired coupling analogous to the Paterno–Buchi and related reactions.[4] We chose *N*-methylphthalimide (NMP) as the electron acceptor since previous investigations[5] indicated that its reactions were localized to the carbonyl group and that the carbonyl oxygen was likely to have nucleophilic properties.

Phenylcyclopropanes are effective donors in photochemical electron transfer reactions[6-9] and evidence indicates that the cyclopropane bond remains intact in the radical cation.[6-10] The susceptibility of phenylcyclopropane (PC) radical cations to nucleophilic attack has been demonstrated[6,7] by the addition of methanol to **6** with subsequent cleavage to **7** which is then reduced by **3** and protonated to give **8**.



Irradiation of NMP and PC in methanol afforded the ether **8** and the hydroxy lactam **9**, establishing that an electron transfer process has taken place and that NMP cannot compete as a nucleophile with methanol.



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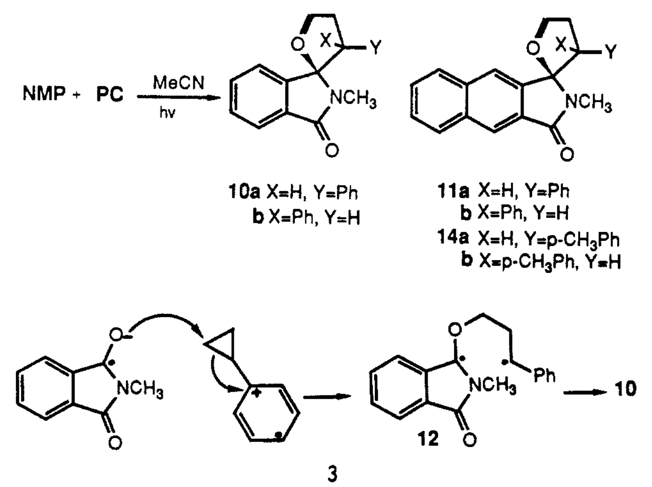
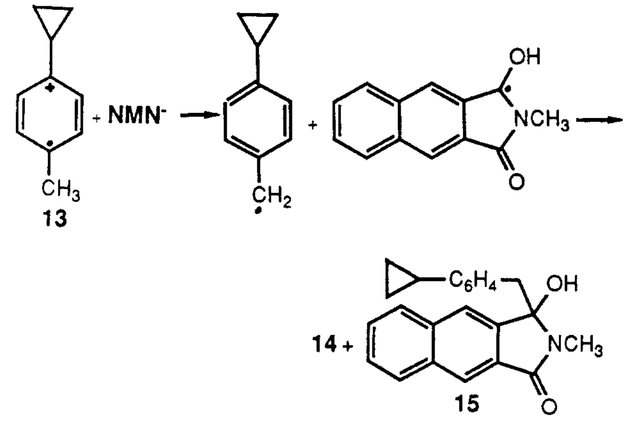
Scheme II



When N-methylphthalimide (NMP) and PC were irradiated in acetonitrile the reaction gave two isomeric products **10**, each in 11% yield. In a similar manner, irradiation of N-methyl-2,3-naphthalimide (NMN) and PC in acetonitrile gave the corresponding pair of naphthalene derivatives in a 1:1 ratio and a combined yield of 56%.[11] The structures of these products were firmly established by ^{1}H NMR, and 2-D NMR confirmed the coupling relationships.

The infrared spectra of **10** and **11** showed a carbonyl absorption at 1690 cm^{-1}. Finally an X-ray crystallographic structure determination confirmed the structure of **11a**.[12] A proposed stepwise mechanism for the formation of **10** (**11**) is outlined in Scheme II although a concerted processes is a distinct possibility.

In the case of (p-methylphenyl)cyclopropane, we observed, in addition to the expected cycloadducts **14**, an equal amount of the photoreduction product **15** which must arise from proton transfer from the **13** to NMN$^{\bullet -}$ followed by coupling of the radical pair. This observation demonstrates that proton transfer remains a viable process in this system and suggests that if the cyclopropane ring in the PC radical cation were not intact, **16** would likely proton transfer to give the allyl radical **17**.



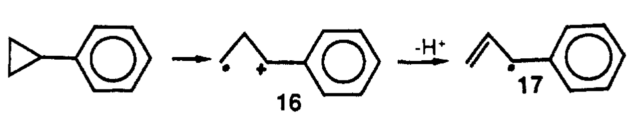
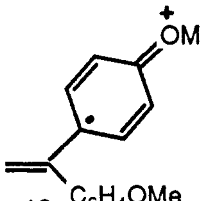


Table I. Fluorescence Quenching Data for Substituted Phenylcyclopropanes

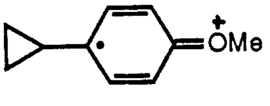
R-Ph-c-C_3H_5	E_{ox}, V^a	ΔG_{ET}, kcal/mol	$k_{q,calcd}$, $\times 10^{-10}$	$k_{q,exptl}$, $\times 10^{-10}$	Φ rel
MeO	1.42	−9.51	1.21	1.94	no reaction
Me	1.57	−6.05	0.986	1.20	0.56
H	1.83	−0.051	0.133	0.089	1
Cl	1.86	0.641	0.073	0.051	0.85
CN	2.17	7.79	$<10^{-5}$	0	no reaction

[a] Vs. SCE; working electrode Au; CH_3CN/0.1 M TEAP.

A comparison of the photoreactivity and fluorescence quenching efficiency of a series of phenylcyclopropanes with NMN shows good correlations of fluorescence quenching efficiencies with ΔG_{ET} (Table I). We observed no reaction with p-cyano-PC, consistent with the fluorescence results, but, surprisingly, p-methoxy-PC, which efficiently quenches NMN fluorescence, affords none of the corresponding adduct. Farid and Mattes[1] have suggested that **18** is unreactive to alcohol nucleophiles because the positive charge in the radical cation resides on oxygen which may also explain the lack of reactivity of **19**.



18



19

In conclusion, we believe that the first general case of a photochemically generated radical anion radical cation pair undergoing cycloaddition has been observed. We are presently looking for other examples of this process and investigations of the mechanism of this reaction are continuing.

Acknowledgment. We thank the National Science Foundation for funds toward the purchase of an X-ray spectrometer and 400-MHz NMR under Grants CHE-84-02155 and DMB-84-20175, respectively.

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(11) All new products showed acceptable NMR, IR, and analytical data. Details will be published in a full paper.

(12) Crystals of **11** were isolated from ethyl ether. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (graphite monochromator). Space group $P2_1/n$, $a = 7.140$ (1) Å, $b = 14.038$ (1) Å, $c = 16.729$ (3) Å, $\beta = 97.28$ (1)°, $Z = 4$. 3239 total data collected to $\theta = 25°$; 1739 data 3s above background. Structure solved with direct methods. Structure refinement by full-matrix least squares. Final $R = 0.040$, $R_w = 0.041$.

Detection and Kinetics of Formation and Disproportionation of the Mixed-Valence Pt_2(II,III) Complex $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$

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Recently the photophysics of the diplatinum(II) complex anion $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ has been the subject of intense study. The primary thrust of this earlier work has been to develop a better understanding of the bonding and energy levels in both the ground and excited states. From quenching measurements being made in parallel with these studies, it is apparent that the excited state $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-*}$ is both a strong oxidant and reductant.[2] Nevertheless, despite this recent spate of published work, little is yet known about the 1-electron-oxidized and -reduced platinum

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