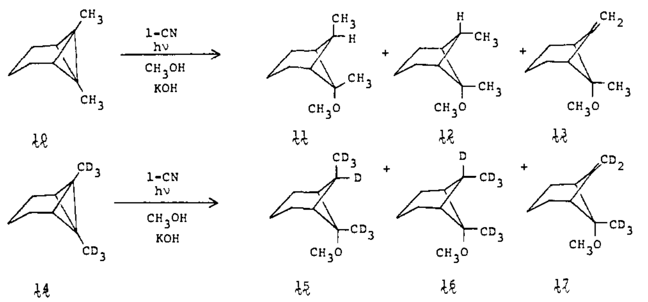
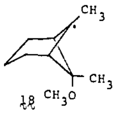
ference NMR spectrum (Figure 2). The coupling constant of 5.9 Hz for H_B with the bridgehead hydrogens firmly established the assignment shown.[7]

Whereas the photodimerization of **4** differed greatly from that of **1**, the addition of nucleophilic solvent to **1** and **4** was very similar. Thus, the use of methanol-*O-d* as nucleophilic solvent in the photosensitized addition resulted in the replacement of H_B of **8** by deuterium.

Upon addition of two methyl groups to **1**, its photoinduced chemistry changed dramatically. Prolonged irradiation of **10** in benzene containing 9,10-dicyanoanthracene (DCA) gave back only starting material, even though **10** quenched the fluorescence of 1-CN and DCA at approximately a diffusion-controlled rate.[11] However, **10** added methanol readily under the photosensitized conditions described above. In contrast to the very clean additions observed with **1** and **4**, **10** gave a complex mixture consisting of 32% of **11**, 7% of **12**, and 40% of **13**.[12] Catalytic hydrogenation of **13** over spongy palladium gave a 3.7:1 ratio of **12**:**11**. The correspondence of the combined yield of **11** and **12** to that of **13** suggested that a disproportionation reaction may have occurred.[13] Irradiation in the presence of methanol-d_4 gave **11**, **12**, and **13** with three deuteriums each, indicating that methanol was not the source of the proton at C-7, as it had been in the photoaddition to **4**. So that the mechanism could be further clarified, **14** was subjected to the reaction conditions to give **15** and **16** with seven deuteriums each and **17** with five deuteriums. This firmly established that the hydrogen (deuterium) at C-7 was obtained from one of the methyl groups and implicated **18** as a critical intermediate. This also elucidated the presence of a major difference in the mechanistic pathways followed by **1**, **4**, and **10**.





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While the experiments discussed above do not differentiate between the initial generation of an exciplex, a charge-transfer complex, or a cation radical–anion radical pair, we prefer to discuss these reactions as occurring via electron transfer (at least for the sensitized addition of nucleophiles).[14] Thus, all of the observed products can be rationalized on the basis of an initially generated bicyclo[1.1.0]butyl-type cation radical[15,16] and 1-CN anion radical. We are continuing to investigate both the synthetic and mechanistic details of the photoinduced reactions of highly strained polycyclic molecules.

Acknowledgment. We are indebted to the National Science Foundation for Grants CHE78-10231 and CHE81-14772, which supported this investigation, and for Grants CHE77-28505 and CHE79-26027, which aided in the purchase of the Enraf-Nonius X-ray Diffractometer and the 300-MHz Nicolet Multinuclear Magnetic Resonance Spectrometer, respectively, which were used in this investigation. We thank M. McGuiggan and Professor L. Pignolet for their help in the X-ray study.

Registry No. 1, 287-13-8; **2**, 78733-48-9; **4**, 32348-63-3; **5**, 81831-74-5; **6**, 81846-98-2; **7**, 81873-88-3; **8**, 81831-75-6; **9**, 81846-99-3; **10**, 33492-27-2; **11**, 81831-76-7; **12**, 81873-89-4; **13**, 81831-77-8.

Supplementary Material Available: Tables of bond distances, bond angles, thermal parameters, and atom coordinates (7 pages). Ordering information is given on any current masthead page.

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[11] The log k_q for the fluorescence quenching of 1-CN by **1**, **4**, and **10** were 10.06, 9.94, and 10.31, respectively.

[12] The spectral properties of **11**, **12**, and **13** were consistent with the assigned structures.

[13] For a balanced disproportionation reaction to occur, an equivalent of hydrogen gas would have to be generated or an associated reduction must occur.

[14] It should be noted that mechanisms are never *proven*; they are only *disproven*.

[15] Theoretical calculations indicate that the cation radical generated by removal of an electron from bicyclo[1.1.0]butane should maintain a structure that is very similar to the parent hydrocarbon: Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5793.

[16] Compounds **1**, **4**, and **10** give up electrons with great ease as demonstrated by their oxidation half-wave potentials vs. a saturated calomel electrode (SCE) at platinum of 1.50, 1.22, and 1.06 V, respectively: Gassman, P. G.; Mullins, M. J., unpublished results.

Magnification of Neighboring-Group Participation in the Solvolytic Generation of Carbocations through the Placement of an Electron-Withdrawing Substituent on the Incipient Cationic Center

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Received March 5, 1982

As part of our general study of the effect of electron-withdrawing substituents on incipient carbocationic centers, we have demonstrated that the cyano function is ambivalent in that it is inductively destabilizing and mesomerically stabilizing when attached directly to a positively charged carbon.[1] We have also shown that the relative contributions of these two effects are a function of the amount of charge on the carbon α to the cyano moiety.[1a,b,f] It occurred to us that certain longstanding and controversial problems of charge delocalization in carbocation chemistry might be simplified through an analysis of analogous systems that differ only in the substitution of an α-cyano group for an α-hydrogen. We had previously demonstrated that stabilization of an incipient carbocationic center could "level" or completely eliminate certain types of neighboring-group participation in solvolysis reactions.[2-4] We now report that destabilization of an incipient carbocationic center can "magnify" the role of an interactive neighboring group and as a result provide data that are more definitive and less controversial.[5]

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[1] (a) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214. (b) Gassman, P. G.; Talley, J. J. *Ibid.* **1980**, *102*, 4138. (c) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, *102*, 7613. (d) Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *Ibid.* **1980**, *102*, 3957. (e) Gassman, P. G.; Saito, K. *Tetrahedron Lett.* **1981**, *22*, 1311. (f) Gassman, P. G.; Talley, J. J. *Ibid.* **1981**, *22*, 5253. (g) We have recently been informed by Professor P. Schleyer that he had supervised an undergraduate who had solvolyzed a derivative of acetone cyanohydrin (E. A. Hyson, 1971). Professor Schleyer has requested that we cite this result and we are pleased to oblige.

[2] Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 2549. Gassman, P. G.; Fentiman, A. F., Jr. *Ibid.* **1969**, *91*, 1545.

[3] Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 2551.

[4] For a detailed discussion of our "tool of increasing electron demand" see: Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; pp 101, 163–175.

[5] Numerous previous examples of the effects of electron-withdrawing substituents on solvolysis reactions have appeared in the literature. However, in those cases where the magnification effect could have been evaluated, the substituents were less proximate than in the present study. Thus, the overall ability of such groups to provide "magnification" of neighboring-group participation was difficult to establish. For examples see: Gassman, P. G.; Marshall, J. L.; Macmillan, J. G.; Hornback, J. M., *J. Am. Chem. Soc.* **1969**, *91*, 4282. Muneyuki, R.; Yano, T. *Ibid.* **1970**, *92*, 746. Lenoir, D. *Tetrahedron Lett.* **1974**, 1563. Farcasiu, D. *J. Org. Chem.* **1978**, *43*, 3878. Grob, C. A. et al. *Tetrahedron Lett.* **1981**, *22*, 835, 1211, 3231. Apeloig, Y.; Arad, D.; Lenoir, D.; Schleyer, P. v. R. *Ibid.* **1981**, *22*, 879. Lambert, J. B.; Mark, H. W.; Holcomb, A. G.; Magyar, E. S. *Acc. Chem. Res.* **1979**, *12*, 317. This last reference is particularly relevant to the present study.

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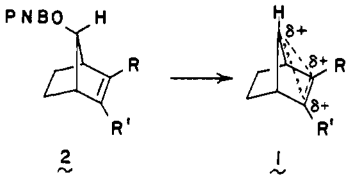
Table I. Rates of Solvolysis of *syn*-7-Cyanobicyclo[2.2.1]hept-2-en-*anti*-7-yl *p*-Toluenesulfonates in 100% 2,2,2-Trifluoroethanol Buffered with 2,6-Lutidine

compd	temp (±0.02), °C	rate, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel} (25 °C)
3a	85.00	$(1.31 \pm 0.01) \times 10^{-3}$	19.7 ± 0.7	−17.9 ± 1.0	
	75.00	$(6.09 \pm 0.05) \times 10^{-4}$			
	65.00	$(1.56 \pm 0.02) \times 10^{-4}$			
	25.00[a,b]	4.20×10^{-6}			1
3b	60.00	$(5.21 \pm 0.16) \times 10^{-3}$	14.5 ± 0.4	−25.8 ± 1.6	
	45.00	$(1.98 \pm 0.06) \times 10^{-3}$			
	30.00	$(5.32 \pm 0.07) \times 10^{-4}$			
	25.00[a]	3.60×10^{-4}			86
3c	0.00	$(1.85 \pm 0.01) \times 10^{-3}$	13.4 ± 0.6	−21.5 ± 1.3	
	−10.00	$(7.72 \pm 0.20) \times 10^{-4}$			
	−20.00	$(2.43 \pm 0.05) \times 10^{-4}$			
	25.00[c]	1.67×10^{-2}			3976

[a] Extrapolated from higher temperatures. [b] A value of 4.34×10^{-6} s^{-1} was previously reported.[1b] [c] Extrapolated from lower temperatures.

In order to establish the validity of the hypothesis outlined above, we chose to test our approach on the once controversial bicyclo[2.2.1]hept-2-en-*anti*-7-yl cation (**1a**).[6,7] We had previously demonstrated that neighboring-group participation by the double bond of **2a** led to a symmetrical transition state in which positive charge was delocalized equally to C-2 and C-3.[8] This was accomplished by comparison of the relative rates of solvolysis of **2a**, **2b**, and **2c**, which were 1, 13.3, and 148, respectively, at 140 °C.[8,9] In order to determine whether relative rate factors resulting from neighboring-group participation could be "magnified", we prepared **3a**, **3b**, and **3c**.[10] Table I lists the rates of solvolysis of **3a**, **3b**, and **3c** in anhydrous 2,2,2-trifluoroethanol buffered with 2 equiv of 2,6-lutidine.[11,12] Inspection of the table shows that the relative rates of solvolysis at 25 °C were 1, 86, and 3976. At 25 °C in 70:30 dioxane–water, the relative rates for **2a**, **2b**, and **2c** were 1, 9.5, and 153. For assurance that these rate ratio differences were not a result of the solvent change from 70:30 dioxane–water to 100% 2,2,2-trifluoroethanol (TFE), the solvolyses of **2a–c** were followed in 100% TFE to give relative rates at 140 °C of 1, 8.8, and 107.[13] This clearly demonstrated that the placement of a cyano group at the incipient cationic center of the system being studied in this test significantly increased the relative rate factors resulting from methyl substitution. *Thus, in closely related systems where a single type of neighboring-group participation is involved, the placement of a strong electron-withdrawing group at the incipient cationic center can magnify the influence of a related series of neighboring groups.*[14]

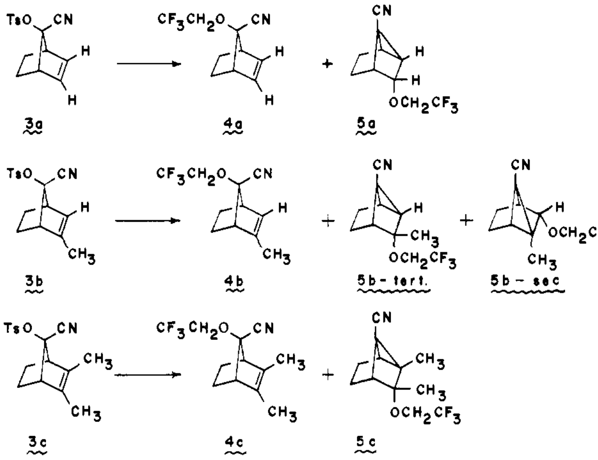


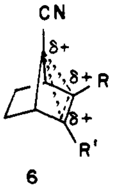
(a) R = R' = H

(b) R = H, R' = CH_3

(c) R = R' = CH_3

While **3a–c** gave the same types of products, the product ratios differed greatly. As previously indicated[1b] **3a** gave 3% of **4a** and 92% of **5a**. 2,2,2-Trifluoroethanolysis of **3b** gave 26% of **4b**, 42% of **5b**-tert, and 28% of **5b**-sec. Lastly, **3c** gave 87% of **4c** and 7% of **5c**. All of the products were stable to the reaction conditions and, as a result, represent the kinetically controlled product mixture. Since the kinetic data leave no doubt about the existence of a symmetrical delocalized transition state, we make the reasonably safe extrapolation that a symmetrical ion, **6**, was gen-





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[7] Brown, H. C.; Bell, H. M. *J. Am. Chem. Soc.* **1963**, *85*, 2324.

[8] Gassman, P. G.; Patton, D. S. *J. Am. Chem. Soc.* **1969**, *91*, 2160. Rates were measured in 70:30 dioxane–water.

[9] Since these rate factors showed a cumulative effect of the methyl substitution rather than a statistical effect, it was concluded[7] and accepted (ref 4, p 61) that the transition state involved symmetrical participation by the double bond.

[10] Compounds **3a**[1b] and **3c** were prepared from the corresponding ketone[8] cyanohydrins in a standard manner.[1] The ketone precursor for the cyanohydrin *p*-toluenesulfonate **3b** was prepared by Swern oxidation (Huang, S. L.; Omura, K.; Swern, D. *J. Org. Chem.* **1976**, *41*, 3329) of the appropriate alcohol.[8] Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds. In all cases the spectral data were consistent with the assigned structures. The stereochemistry of the intermediate cyanohydrins was established through a high-dilution IR hydrogen-bonding study.[1b]

[11] No significant difference in rate resulted when the equivalents of buffer used was varied from 1 to 3.

[12] Because of the rather significant differences that existed for the ΔH^{*} and ΔS^{*} values for **3a**, **3b**, and **3c**, respectively, large temperature extrapolations resulted in major changes in the rate ratios. Thus, at 140 °C (55 °C above the highest measured rate) the ratio was 1:8:213, while at −75 °C (55 °C below the lowest measured rate) the ratio was $1:620:8.1 \times 10^{5}$. As a result we felt that rates were best compared near the midpoint of the experimental results (25 °C).

[13] The measured and/or extrapolated rates for **2a**, **2b**, and **2c** at 140 °C were 2.59×10^{-5}, 2.27×10^{-4}, and 2.78×10^{-3} s^{-1}, respectively.

[14] We stress that this test is restricted to closely related neighboring groups in which the mechanism of all of the substrates being compared remains the same. In systems that vary greatly in the type of neighboring-group participation involved and in the relative rates of ionization (i.e., bicyclo[2.2.1]hept-7-yl *p*-toluenesulfonate and bicyclo[2.2.1]hept-2-en-7-yl *p*-toluenesulfonate[1b]) the placement of a strong electron-withdrawing group α to the leaving group may result in a complete change in mechanism of one or more of the solvolyses being studied. In such situations, the test would be invalid. Fortunately, in most situations of this type, the rate differences of the parent systems are sufficiently large that the test is not needed.

erated. The product ratio would then be determined by differences in transition-state energies for the reaction of **6** with 2,2,2-trifluoroethanol. Since the product ratios indicate relatively small energy differences in these transition-state energies, the cause of the differences in product ratio is difficult to ascertain.

We are applying our approach of the magnification of neighboring-group participation to other, more controversial situations involving carbocations that may be stabilized by intramolecular interactions with neighboring groups.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE81-14772, which supported this investigation.

Registry No. 2a, 16558-31-9; **2b**, 24577-73-9; **2c**, 24577-09-1; **3a**, 74816-06-1; **3b**, 81897-98-5; **3c**, 81897-99-6; **4a**, 74816-17-4; **4b**, 81898-00-2; **4c**, 81898-01-3; **5a**, 74816-16-3; **5b**-*tert*, 81898-02-4; **5b**-*sec*, 81898-03-5; **5c**, 81898-04-6.

Matrix Isolation Infrared Spectra of Oxy(tetraphenylporphyrinato)iron(II)

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Although ferrous porphyrins are highly important as models of hemoglobin and myoglobin, simple (unprotected) ferrous porphyrins such as Fe(TPP) (TPP: tetraphenylporphyrinato anion) cannot bind molecular oxygen reversibly under normal conditions since they are rapidly and irreversibly oxidized to form μ-oxo dimers. So that this oxidation could be prevented, "protected" porphyrins such as picket-fence and cap porphyrins have been synthesized and their oxygenation reactions studied extensively.[1] We now present the first IR evidence for the formation of "base-free" O_2 adducts of "unprotected" ferrous porphyrins with use of matrix cocondensation techniques. Since Fe(TPP) itself is highly air-sensitive, we have developed the following procedure to prevent its oxidation.

A stable, "base-bound" complex, Fe(TPP)(pip)$_2$ (pip: piperidine),[2] was placed inside the Knudsen cell of our matrix isolation system and heated in a vacuum of 10^{-6} torr at 370 K for 4 h until the vacuum gauge indicated complete dissociation of the base from the complex. The "base-free" Fe(TPP) thus obtained was vaporized from the Knudsen cell at 430 K and cocondensed with pure Ar or O_2 diluted in Ar on a CsI window that was cooled to ~15 K by a CTI Model 21 closed-cycle helium refrigerator. The IR spectra were measured on a Beckman Model 4260 IR spectrophotometer with a 25 cm^{-1}/in. chart expansion and 5 cm^{-1}/min chart speed.

Trace A of Figure 1 shows the IR spectrum of Fe(TPP) in an Ar matrix. As is expected, this spectrum is very similar to those of Co(TPP)[3] and Mn(TPP)[4] because the spectra in the 1600–500 cm^{-1} region are dominated by the TPP vibrations. When Fe(TPP) vapor was cocondensed with $^{16}O_2$/Ar ($^1/_{10}$), two new bands were observed at 1195 and 1106 cm^{-1}, as is seen in trace B. Similar spectra were obtained in pure $^{16}O_2$ amd more diluted $^{16}O_2$/Ar ($^1/_{300}$ – $^1/_{1000}$) matrices. These results suggest that the O_2 adduct has the 1:1 (O_2/Fe) stoichiometry. The bands at 1195 and 1106 cm^{-1} were shifted to 1127 and 1043 cm^{-1}, respectively, by the $^{16}O_2$–$^{18}O_2$ substitution (trace C). The observed isotopic shifts of these bands (68 and 63 cm^{-1}, respectively) are in perfect agreement with that expected for a perturbed diatomic molecule. Thus, we assign both bands to the $\nu(O_2)$ of "base-free" adduct, Fe(TPP)O_2.

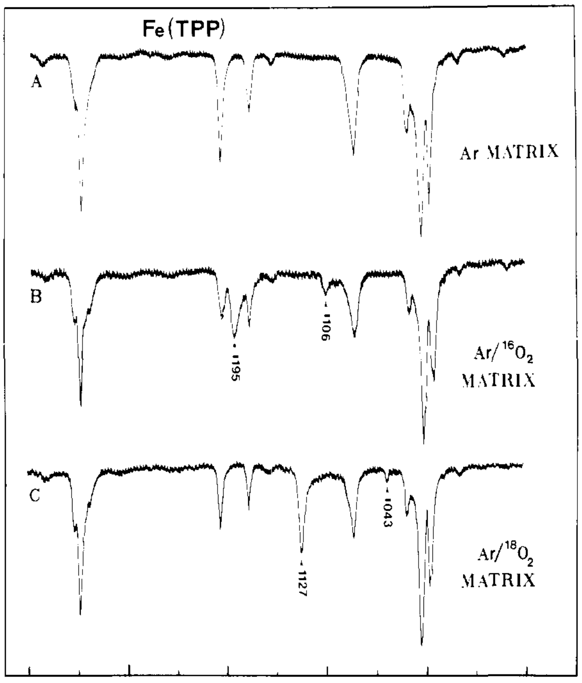

Figure 1. Infrared spectra of (A) Fe(TPP) in Ar matrix, (B) Fe(TPP) cocondensed with $^{16}O_2$/Ar ($^1/_{10}$), and (C) Fe(TPP) cocondensed with $^{18}O_2$/Ar ($^1/_{10}$) at ~15 K. The purity of $^{18}O_2$ gas was 95.2%.

The appearance of two $\nu(O_2)$ bands for Fe(TPP)O_2 is intriguing. The weaker band at 1106 cm^{-1} is not due to Fe(TPP)(pip)O_2 since exactly the same spectrum was obtained when Fe(TPP)(py)$_2$ was used as the starting complex. The possibility of Fermi resonance with the first overtone of the ν(FeO)[5] or a porphyrin mode[6] is remote since both $^{16}O_2$ and $^{18}O_2$ adducts exhibit the same number of bands without any shifts of the TPP vibrations. The matrix site effect does not seem to be responsible since the intensity ratio of the two bands remains unchanged in a variety of matrix environments. In fact, a thin film of Fe(TPP) reacted with O_2 exhibits spectra similar to those shown in Figure 1. If this film is warmed up, the 1195-cm^{-1} band gains intensity at the expense of the 1106-cm^{-1} band. Although the latter disappears completely at ~100 K, recooling to ~15 K recovers its original intensity. These observations suggest that there are two isomers of Fe(TPP)O_2 and that isomer I (1195 cm^{-1}) is stable up to 240 K (at which it decomposes), whereas isomer II (1106 cm^{-1}) is converted to isomer I by raising the temperature up to ~100 K. These two isomers may differ in the spin state of Fe(II) or the Fe–O–O geometry or both. At present, a more detailed and thorough study is in progress to understand the nature of these isomers.

It should be noted that the order of $\nu(O_2)$ of "base-free" adducts is Co(TPP)O_2 (1278 cm^{-1})[3] > Fe(TPP)O_2 (1195/1106 cm^{-1}) > Mn(TPP)O_2 (983 cm^{-1}).[4] The O_2 in Mn(TPP)O_2 is approximated by the peroxide (O_2^{-2}) ion.[7] The O_2 of "base-free" Co(TPP)O_2 is much more positive than that of "base-bound" Co(TPP)(N-MeIm)O_2 (1142 cm^{-1}),[8] which is regarded as the superoxide (O_2^-) type.[9] Thus, we conclude that the negative charge on the O_2 of "base-free" Fe(TPP)O_2 is between these two extremes and probably close to O_2^-. Although the nature of the Fe–O_2 interaction in "base-bound" adducts is controversial,[10] the present IR

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