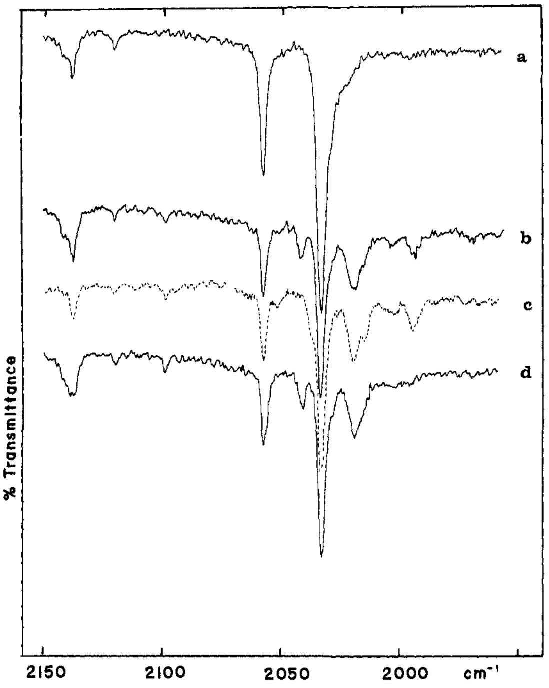

Figure 1. Infrared spectra of an argon matrix of $HCo(CO)_4$ containing 10 mol % of H_2 on liquid-helium-cooled NaCl: (a) immediately after deposit; (b) after 5 min of photolysis with a low-pressure mercury lamp; (c) after 5 min of photolysis of a similar matrix containing 10 mol % D_2; (d) after 25 min of exposure to the full emission of the Nernst glower.

absorptions due to $Co(CO)_4$. When deuterium-containing matrices of $HCo(CO)_4$ are photolyzed, the band at 2043 cm^{-1} does not appear. Rather, a band at 2038.3 cm^{-1} is observed as a shoulder on the principal absorption of $HCo(CO)_4$. The normal mode which affords the absorption at 2038.3 cm^{-1} undoubtedly correlates to the mode that absorbs at 2042.6 cm^{-1} in the hydrogen-containing matrix. The shift in the carbonyl modes upon deuteration is a well-known phenomenon among the hydrides.[8] Also, as deuterium-containing matrices of $HCo(CO)_4$ are photolyzed, a minor band grows in at 2052.5 cm^{-1}, which can be assigned to the low-frequency A_1 mode of $DCo(CO)_4$.[6] At the same time the intensity ratio of the low-frequency A_1 mode of $HCo(CO)_4$ to its E mode declines. The modes of E symmetry of both $HCo(CO)_4$ and $DCo(CO)_4$ appear at the same frequency. These data are consistent with isotope exchange between $HCo(CO)_4$ and D_2.

The behavior of $HCo(CO)_4$ in hydrogen-containing matrices is consistent with the following scheme:

$$HCo(CO)_4 \overset{254\ nm}{\rightleftharpoons} HCo(CO)_3 + CO$$

$$HCo(CO)_3 + H_2 \underset{254\ nm}{\rightleftharpoons} H_3Co(CO)_3$$

The bands at 2100 and 2043 cm^{-1} are assigned to the trihydride of cobalt tricarbonyl. If the band at 2021 cm^{-1} also belongs to the same species, then the $H_3Co(CO)_3$ is a meridional isomer analogous to $H_3Co(PPh_3)_3$.[9] The evidence points to the oxidative addition of hydrogen because (1) isotope exchange implies the hydrogen atom of the hydride becomes equivalent to those of the incoming hydrogens, (2) added deuterium perturbs the carbonyl modes in a similar fashion to other hydrides, (3) the frequencies of the carbonyl modes are similar to other coordinatively saturated cobalt carbonyls, and (4) the bands due to $H_3Co(CO)_3$ do not decline when the matrix is exposed to the visible radiation of the glower. On the other hand, $Co(CO)_4$ does not appear to react with H_2 under the same conditions. In CO matrices, the only observed product is $Co(CO)_4$, even in the presence of hydrogen.

The identification of another cobalt carbonyl hydride need not shake the currently held mechanisms for oxo chemistry.[10] $H_3Co(PPh_3)_3$ is readily decomposed in CO-containing atmospheres, and the same chemistry is suggested for $H_3Co(CO)_3$.[11] As $HCo(CO)_4$ is rarely handled except in CO atmospheres, $H_3Co(CO)_3$ may be present in inconsequential amounts. High-pressure studies of cobalt carbonyls by Whyman[12] and by Vidal and Walker[13] gave no evidence for $H_3Co(CO)_3$ although Whyman's study of iridium carbonyls did show the formation of a trihydridoiridium complex in a pure hydrogen atmosphere.[14]

Registry No. $H_3Co(CO)_3$, 81875-87-8; $HCo(CO)_4$, 16842-03-8.

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(12) Whyman, R. *J. Organomet. Chem.* **1974**, *81*, 97-106.

(13) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1981**, *20*, 249-254.

(14) Whyman, R. *J. Organomet. Chem.* **1975**, *94*, 303-309.

Photochemistry of Saturated Hydrocarbons. Mechanistic Changes as a Function of Methyl Substitution in the Photosensitized Reactions of the Tricyclo[4.1.0.0^{2,7}]heptyl System

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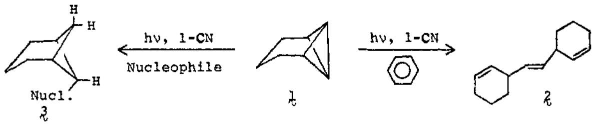
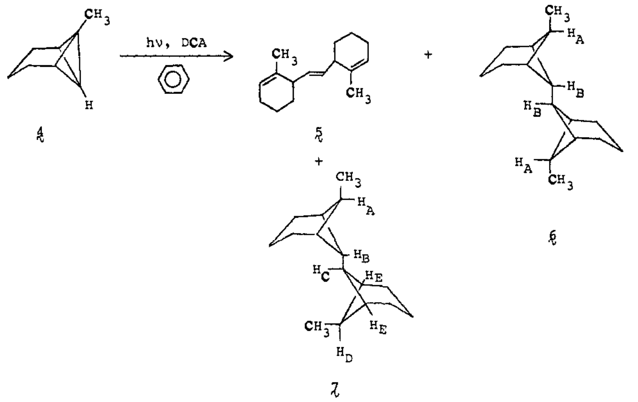
Received February 1, 1982

Recently, we reported an unprecedented series of photoinduced transformations of the saturated hydrocarbon tricyclo[4.1.0.0^{2,7}]heptane (**1**).[2] In the absence of nucleophiles, irradiation of a solution of **1** and the photosensitizer 1-cyanonaphthalene (1-CN)[3] gave the dimer **2**, while in the presence of nucleophiles (i.e., methanol, water, cyanide ion) only **3** was obtained. We now report that methyl substitution on the tricyclo[4.1.0.0^{2,7}]heptyl skeleton can dramatically alter the paths of the photoinduced reactions of this hydrocarbon.



3 1 2

Irradiation of **4** in benzene containing 9,10-dicyanoanthracene (DCA) through Pyrex with a 450-W medium-pressure Hanovia lamp for 8 h gave a mixture of **5** (17%), **6** (16%), and **7** (5%), in contrast to the 90% of **2** obtained from **1**. The structure of **5**



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(1) University of Minnesota Dissertation Fellow, 1980-1981; Procter and Gamble Foundation Fellow, 1981-1982.

(2) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977.

(3) 1-Cyanonaphthalene and 9,10-dicyanoanthracene have been used interchangeably as sensitizers in this photoinduced dimerization.

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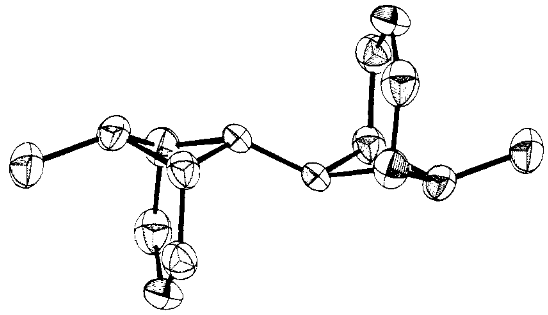


Figure 1. ORTEP drawing of **6** with hydrogens omitted for clarity.

was established through a comparison of its spectral properties with those of **2**.[4] The structure of **6** was established as that of a symmetrical dimer on the basis of its mass spectrum and its simplistic ^{13}C NMR (($CDCl_3$) δ 39.59 (d), 37.48 (d), 34.93 (d), 20.06 (t), 14.38 (t), 11.17 (q)). The exact structure of the crystalline dimer **6**, mp 114–116 °C, was established by single-crystal X-ray analysis.[5] Figure 1 is an ORTEP drawing of **6**. The structure of **7** proved to be more difficult to establish. ^1H NMR showed a complex series of multiplets with two methyl doublets appearing at δ 0.80 and 1.15, while the presence of a partially symmetric dimer was established by ^{13}C NMR (δ 41.32 (d), 39.03 (d)*, 37.43 (d)*, 35.97 (d), 34.85 (d)*, 34.11 (d), 24.89 (t), 20.14 (t)*, 16.97 (q), 14.78 (t), 14.43 (t)*, 11.17 (q)*).[6] The mass spectral cracking pattern for **7** was virtually identical with that of **6**. This, combined with the NMR data, suggested the presence of the same skeletal system with a variance in the stereochemistry at the junction of one of the two bicyclo[3.1.1]heptyl moieties, of one of the methyl groups, or at both positions. Through the use of 300-MHz ^1H NMR, it was established that the CH_3, H_A, and H_B resonances of **6** appeared at δ 0.95, 2.11, and 2.16, respectively. For **7**, one methyl group, H_A, and H_B appeared at δ 0.92, 2.11, and 2.13, respectively, indicating that the top half of **7** had the same stereochemistry as both halves of **6**. Through analysis of the 300-MHz ^1H NMR of **7** with H_B decoupled, it was determined that H_C was coupled to H_E by 6 Hz.[7] Thus, **7** must differ from **6** only in the stereochemistry of the one methyl group as shown.

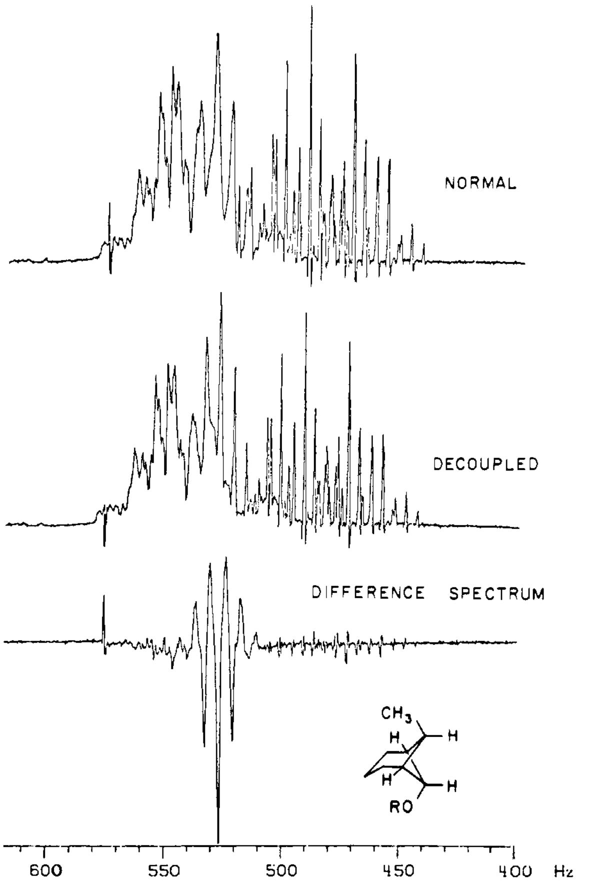
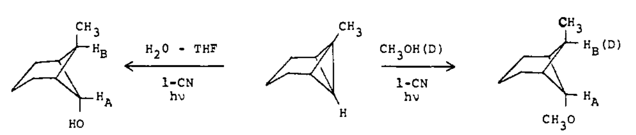


Figure 2. Region from 400 to 600 Hz downfield from Me_4Si in the 300-MHz ^1H NMR spectrum of **9**. The top spectrum is undecoupled (normal). The middle spectrum is in the same region with the methyl group at δ 0.98 decoupled. The bottom spectrum is a difference spectrum with the portion of the spectrum above the line representing the spectrum of the hydrogen α to the methyl group in the undecoupled spectrum, while that portion of the spectrum below the line represents the spectrum of the hydrogen α to the methyl group when the methyl group has been decoupled.

Irradiation of a methanolic solution of **4** containing 1-CN as the photosensitizer and 0.1% potassium hydroxide for 10 h through Vycor gave 93% of 6-methoxy-7-methylbicyclo[3.1.1]heptane (**8**) (VPC yield vs. an internal standard; isolated yield 56%).[8,9] Similar irradiation of **4** in 1:9 water–tetrahydrofuran gave **9** (90% yield by VPC vs. an internal standard; 70% isolated yield), mp 98–99 °C.[9] The anti-Markovnikov additions of methanol and water to **4** were readily established by both the ^1H and ^{13}C NMR spectra of **8** and **9**.[10] The stereochemistry of H_A in both **8** and **9** was determined on the basis of the coupling constant to the bridgehead protons (J = 6.0 and 5.9 Hz, respectively, for **8** and **9**).[7] The stereochemistry of H_B was established through the use of a dif-



9 **4** **8**

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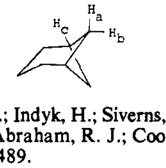
[4] ^1H NMR ($CDCl_3$) δ 5.40–5.55 (2 H, m), 5.30 (2 H, d of d), 2.35–2.65 (2 H, m), 1.1–2.3 (18 H, m with methyl peak as a singlet at 1.60); ^{13}C NMR ($CDCl_3$) δ 135.38 (s), 133.62 (d), 122.34 (d), 42.54 (d), 29.83 (t), 25.41 (t), 22.43 (q), 19.06 (t).

[5] The white crystals of $C_{16}H_{26}$ belonged to the monoclinic space group $P2_1/c$. The measured cell constants a = 11.045 (4) Å, b = 10.593 (2) Å, c = 12.741 (7) Å, and β = 115.21 (4)° gave a calculated density of 1.075 g/cm³ for four molecules in the unit cell at ambient temperature. Data were collected on a fully automated Enraf-Nonius CAD 4 diffractometer with a variable rate ω–2θ scan technique and graphite-monochromatized Cu Kα radiation (λ = 1.54184 Å). After Lorentz and polarization corrections, 1202 of 2835 unique reflections (42%) with 2θ = 0–156° were observed for $[F_o^2 > 2(\sigma(F_o))^2]$. A combination of direct methods and difference Fourier synthesis was used to locate all non-hydrogen atoms. Thermal anisotropic refinement was applied to all non-hydrogen atoms. The positions of all hydrogen atoms were calculated and refined with fixed isotropic thermal parameters by full-matrix least-squares analysis. The unweighted R factor for the structure was 0.068. All calculations were carried out on a PDP 11/34 computer with the Enraf-Nonius SDP programs. This crystallographic computing package is described by Frentz (Frentz, B. A.) In "Computing in Crystallography"; Schenck, H., Olthof-Hazekamp, R., Van Konigweld, H., Bessie, G. S., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

[6] Those values indicated with an asterisk match closely the positions of the carbon resonances of **6**. It should be noted that both **6** and **7** are reduction products. No biphenyl was observed and the use of benzene-d_6 as solvent failed to give any deuterium incorporation into either **6** or **7**. Thus, it is thought that **5** was the most likely source of the hydrogens involved in the reduction.

[7] For the bicyclo[3.1.1]heptyl ring system the coupling constant between H_a and H_c has been found to be 0 Hz, whereas the coupling between H_b and H_c is on the order of 6 Hz.



Abraham, R. J.; Cooper, M. A.; Indyk, H.; Siverns, T. M.; Whittaker, D. *Org. Magn. Reson.* **1973**, *5*, 373. Abraham, R. J.; Cooper, M. A.; Salmon, J. R.; Whittaker, D. *Ibid.* **1972**, *4*, 489.

[8] The photochemical conversions of **4** into **8** and **9** were run on less than 1 g of **4**. We believe that, on a larger scale, where losses by distillation would be minimized, isolated yields would approximate VPC yields.

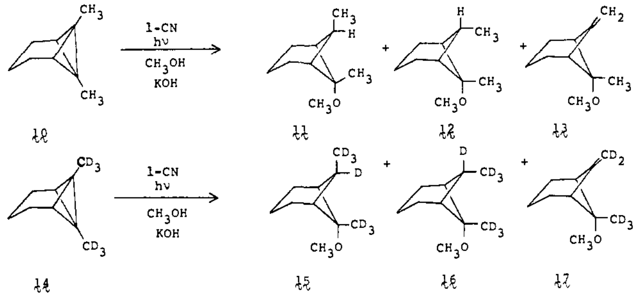
[9] Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds.

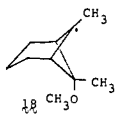
[10] For example **8** showed the following: ^1H NMR ($CDCl_3$) δ 3.45 (1 H, t), 3.25 (3 H, s), 2.45–2.25 (3 H, br m), 1.90–1.50 (6 H, m), 0.95 (3 H, d); ^{13}C NMR ($CDCl_3$) δ 76.18 (d), 56.08 (q), 40.32 (d), 26.81 (d), 19.29 (t), 14.31 (t), 4.51 (q).

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**.





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.