(2) by maintaining a constant fluence while shortening the pulse length. Results from case 1 experiments, for both long and short laser pulses, are consistent with what would be expected for simple IRMP dissociation. Product yield (total product ion abundance divided by parent ion plus product ion abundances) increases with fluence[8,13] as shown in Figure 1. Branching fractions (individual product yield divided by total product yield) of higher energy products increase with fluence[13] (intensity) at the expense of the lowest energy channel, see[14] Figure 2. However, results from case 2 experiments are completely unexpected. Inspection of Figure 1 shows that, for long and short laser pulses of equal fluence, the short pulse (higher intensity) results in *lower* product yield. This is surprising because the product yield for the short pulse would not be expected to decrease.[8,13,15] To our knowledge there are no previous reports[16] of such behavior.

These results can be explained, however, by a stepwise mechanism that introduces intermediate **2** in the absorption ladder (Figure 3). The lifetime for unimolecular rearrangement of activated **1** to **2** should be[17] comparable to the length of the short laser pulse (200 ns). If **1** has a smaller steady-state cross section for absorption than **2**, the yield for the short pulse will decrease because the more strongly absorbing structure **2** is not present for most of the laser pulse. Presumably the same amount of **1** decomposes from both length laser pulses. It should also be noted that significant decomposition occurs after the laser pulse is completed.[13] Since it is impossible to detect production of **2** (same mass to charge ratio as **1**), the short pulse appears to have a lower product yield. For the long pulse, the higher yield of detectable products arises because of an increased number of ions with structure **2** *during* the laser pulse. If structure **2** has a larger absorption cross section than **1**, the overall photon absorption is greater, leading to a higher product yield.

In summary, IRMP dissociation of butyrophenone cation unexpectedly displays a lower yield for a shorter laser pulse. This is inconsistent with the generally accepted model for IRMP dissociation of a single structure, which would predict a dissociation yield depending only on the number of photons and not on their rate of delivery.[8,13] These results are consistent, however, with a stepwise mechanism for the McLafferty rearrangement in which the butyrophenone molecular cation is formed initially and then, when energized, isomerizes to the distonic ion. Subsequent activation of the distonic ion yields products. These experiments represent the first spectroscopic evidence for the simultaneous existence of a distonic ion and the molecular cation.

Acknowledgment. We are grateful to the National Science Foundation for support of this work. The San Francisco Laser Center provided the cw CO_2 laser.

Registry No. Butyrophenone, 495-40-9.

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[14] Comparable results are obtained for the long (4 μs) laser pulse.

[15] This phenomenon is not a result of inefficient ion trapping due to a larger kinetic energy of product fragments formed in the short-pulse experiment. A plot essentially identical with Figure 1 can be generated by using (1 − parent ion fraction). In other words, parent ion decomposition (which is independent of fragment ion kinetic energy) mirrors the product yield behavior displayed in Figure 1.

[16] A change in fragment ion product distribution from benzene ions formed by UV multiphoton ionization with shortened (20 ps) laser pulses has been observed. This was attributed to insufficient time, during the laser pulse, for complete stepwise fragmentation of the benzene ion. Hering, P.; Maaswinkel, A. G. M.; Kompa, K. L. *Chem. Phys. Lett.* **1981**, *83*, 222.

[17] The energy-dependent unimolecular rate constant for **1** → **2** can vary from 0 at threshold up to about 10^{10} s^{-1} at energies that are still below the threshold for other reactions. In general, however, a rate constant of ca. 10^7 s^{-1} would be expected for medium-sized molecules or ions within a few kilocalories per mole (1 infrared photon) of a modest critical activation energy (ca. 10 kcal/mol). See: Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: New York, 1972.

A New Photochemical Method for Selective Fluorination of Organic Molecules

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While excellent synthetic methods exist for the preparation of perfluorinated organic compounds,[1] the techniques available for selective fluorination are relatively few in number. Broadly speaking, useful reagents for selective fluorination fall into two classes:[2] elemental fluorine[3,4] and compounds prepared either directly from it (acyl hypofluorites,[4,5] fluoroxysulfate,[6] halogen fluorides,[7] and *N*-fluoro compounds[8]) or from other strong oxidants (e.g., $FClO_3$, prepared from $HSO_3F/KClO_4$), and weak oxidants derived from fluoride, such as HF, KF and other metal fluorides, BF_4^-, COF_2, and SF_4. While the range of available techniques is somewhat limited, the need for selectively fluorinated compounds, particularly for biomedical applications,[9] has made their use extremely productive.

We report a new method for selective fluorination, in which oxidizing equivalents are supplied by an illuminated semiconductor (titanium dioxide) and the fluorinating agent is F^-. This method employs safe, easily handled reagents and obviates the need for elemental fluorine and its derivatives. It is applicable to easily oxidized organic substrates, particularly those that form stable carbocations upon oxidation, as well as olefins, phosphines, and phosphites. In a typical reaction, 5 mmol of the substrate is loaded into a 10-mm-diameter borosilicate glass or translucent Teflon FEP tube with an equal weight of rutile TiO_2 powder; 5 mL of acetonitrile and a stoichiometric quantity (10 mmol) of AgF are added.[10] The mixture is deaerated with argon and then illuminated at ambient temperature with a mercury-xenon lamp, typically for 1-2 days. During the course of the reaction, Ag^+, which serves as a scavenger for conduction-band electrons, is reduced to elemental silver. The TiO_2/Ag particles are then recovered from the reaction mixture by filtration. Table I shows the results of some representative photochemical fluorination reactions using TiO_2 and AgF. In almost all cases, only a single fluorinated compound is produced. Control experiments establish that TiO_2, AgF, and light are all essential components of the reaction.

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Table I. Photochemical Fluorination Reactions Using TiO_2/AgF

compd	product[a]	yield,[a] %	^{19}F NMR[b]	*m/z*
1, $(C_6H_5)_3CH$	$(C_6H_5)_3CF$	57	−126.5 (s)[c]	262
2, $(C_6H_5)_2CH_2$	$(C_6H_5)_2CHF$	15	−169.0 (d),[d,e] $J_{HF} = 24$ Hz	186
3, $(CH_3)_2CH(NO_2)$	$(CH_3)_2CF(NO_2)$	47	−112.5 (m)[f] $J_{HF} = 21$ Hz	107
4, $(C_6H_5)_2C{=}CH(C_6H_5)$	$(C_6H_5)_2CFCHF(C_6H_5)$	7	−160 (t, $J_{FF} = J_{HF} = 17$ Hz;[g] −180 (dd), $J_{HF} = 46$ Hz	294
5, $(C_6H_5)_3P$	$(C_6H_5)_3PF_2$	66	−37.5 (d), $J_{PF} = 663$ Hz[c]	300
6, $(CF_3CH_2O)_3P$	$(CF_3CH_2O)_3PF_2$	31	−77.2 (t), $J_{HF} = 8$ Hz;[c] −59 (d), $J_{PF} = 762$ Hz	347
7, $(C_2H_5O)_2P(O)H$	$(C_2H_5O)_2P(O)F$	52	−81.8 (d), $J_{PF} = 960$ Hz[c]	156
8, $(CH_3)(C_6H_5)_2CCOOH$	$(CH_3)(C_6H_5)_2CF$	64	−136 (q), $J_{HF} = 21$ Hz	200
9, $(C_2H_5)(C_6H_5)CHCOOH$	$(C_2H_5)(C_6H_5)CHF$	17	−176.5 (dt), 138 $J_{HF} = 23$ Hz, $J_{HF} = 46$ Hz	138

[a] Products were identified by ^{19}F NMR and mass spectral analyses. Yields reported are from integration of NMR spectra and do not represent isolated yields. [b] Parts per million upfield from $CFCl_3$; 4-fluorobenzophenone and 2,2,2-trifluoroacetophenone were used as internal NMR standards. Assignments were consistent with literature values. [c] Reference 11. [d] Reference 8. [e] $(C_6H_5)_2CHF$ is the only fluorinated product detected when 2 equiv of AgF is used. With 4 equiv of AgF, $(C_6H_5)_2CHF$ is formed in 10% yield and $(C_6H_5)_2CF_2$ (NMR −85.5 ppm (s); *m/z* = 204) is formed in 26% yield.[h] [f] Reference 13. [g] The apparent triplet ($J = 17$ Hz at −160 ppm) is consistent with assignments for $(C_6H_5)_2CFCH_2F$ and $(C_6H_5)_2CF$-CF_2H, ref 14. [h] Reference 12.

Table II. Reactivity vs Oxidation Potential for Carboxylic Acids

compd	E_p (at Pt, V vs SCE)	product	yield, %
11, $(C_6H_5)_3CCOOH$	+1.02[a]	$(C_6H_5)_3CF$	37
12, $(C_6H_5)_2CHCOOH$	+1.27[a]	$(C_6H_5)_2CHF$	21
13, $(C_6H_5)CH_2COOH$	+1.43[a]	no reaction	
14, $(C_6H_5)COOH$	ca. +2.0[b]	no reaction	

[a] Reference 27. [b] Reference 28.

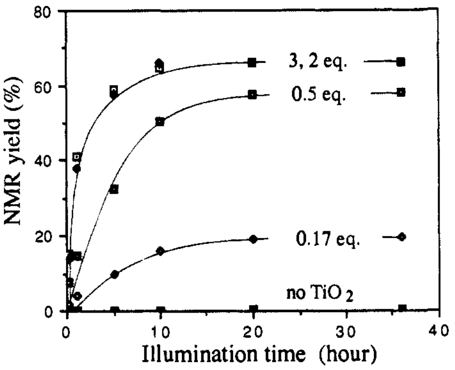

Figure 1. Yield of $(C_6H_5)_3PF_2$ vs time as a function of the amount of TiO_2 (0.00, 0.17, 0.50, 2.00, and 3.00 mol of TiO_2 per mol of $(C_6H_5)_3P$) used. Reactions were run with unfiltered radiation from a 200-W mercury lamp, in 5-mm-diameter pyrex NMR tubes containing 20 mg of $(C_6H_5)_3P$, 20 mg of AgF, 5 mg of KF, 0.5 mL of CD_3CN, and the appropriate quantity of TiO_2; 10 μL of C_6F_6 was added as an internal NMR standard.

Figure 1 shows a plot of product yield vs time for the fluorination of triphenylphosphine, as a function of the amount of TiO_2 photocatalyst used. Fluorination of the substrate occurs in competition with photochemical decomposition of AgF; both processes result in deposition of Ag on the TiO_2 particles and, in the absence of photocatalyst, on the walls of the reaction tube. The product yield and the initial rate of product formation are proportional to the amount of TiO_2 when 0.17 or 0.5 mol of TiO_2 per mol of $(C_6H_5)_3P$ is used. With excess TiO_2, however, the product yield appears to be limited by competitive photodecomposition of AgF on the semiconductor surface. Experiments reported in Tables I and II were performed under conditions where TiO_2 was in excess, i.e., 2–3 mol per mol of substrate.

Titanium dioxide has been studied extensively as an oxidative photocatalyst, e.g., for photo-Kolbe reactions,[15] oxygenation of olefins,[16] amines,[17] and lactones,[18] and mineralization of organic pollutants.[19] While the valence-band potential of TiO_2 is sufficiently positive in some media (e.g., in anhydrous HF) to oxidize F^- to F_2,[20] in acetonitrile solutions the bands are shifted to more negative potentials.[21] Because of this shift, F_2 cannot be evolved photoelectrochemically in acetonitrile,[22] and it is therefore unlikely that it is an intermediate in the reactions described here.

There is substantial evidence from previous work[15-18,23] that, in nonaqueous solvents, photooxidation of organic substrates involves direct electron transfer to the semiconductor particle. The mechanism of photochemical fluorination therefore most likely involves the attack of F^- on either a radical cation or carbocation produced at the semiconductor surface. The fluorination of 3,3,3-triphenylpropionic acid (**10**) according to reaction 1 supports

$$(C_6H_5)_3CCH_2COOH \xrightarrow[AgF]{TiO_2,\ h\nu} (C_6H_5)_2CFCH_2(C_6H_5) \quad (1)$$

this hypothesis; the observed fluorinated product[24] is consistent with phenyl group migration in the radical $((C_6H_5)_3CCH_2^{\bullet})$ generated by oxidative decarboxylation of **10**.[25] For substrates such as **1** and **2**, the carbocation pathway (2) is quite plausible

$$RH \xrightarrow[e^-]{} RH^{\bullet +} \xrightarrow[H^+]{} R^{\bullet} \xrightarrow[e^-]{} R^+ \xrightarrow{F^-} RF \quad (2)$$

since the $R^{\bullet/+}$ potentials (−0.64 and −0.28 V, respectively[26]) are considerably negative compared to the TiO_2 valence-band potential. Interestingly, other easily oxidized compounds, such as

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(24) Yield: 61%. ^{19}F NMR: −144.7 ppm (t, $J_{HF} = 24$ Hz). ^1H NMR: 3.42 (d, $J_{HF} = 24$ Hz), 7.2 ppm (m). MS: *m/z* = 276.

(25) The 2,2,2-triphenylethyl radical is known to rearrange rapidly, e.g., under conditions of Kolbe electrolysis (Breedeweld, H.; Kooyman, E. C. *Recl. Trav. Chim. Pays-Bas* **1957**, *76*, 297), even in the presence of efficient free-radical traps (Kaplan, L. *J. Am. Chem. Soc.* **1966**, *88*, 4531).

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3, **5**, **6**, and **7**, which cannot readily form carbocations, are also reactive.

Table II illustrates the relationship between reactivity and oxidation potential for a series of carboxylic acids. While **11** and **12** are fluorinated, **13** and **14** are recovered unchanged from the reaction mixture. In acetonitrile/tetraethylammonium fluoride solutions, the valence-band potential of TiO_2 is +1.0 V vs SCE;[22] protonation of the surface by **11**–**14** will cause a shift to more positive values. Therefore, the observed reactivity threshold of ca. +1.3 V is consistent with the location of the valence-band potential in this medium. Adjusting this threshold to more positive values, by deliberately protonating the semiconductor surface, or by using more oxidizing photocatalysts (e.g., SnO_2, which has a valence-band potential about 1 V more positive than that of TiO_2[29,30]), may significantly expand the range of molecules into which fluorine can be introduced by this method. Experiments along these lines are currently in progress.

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Ab Initio Calculations of the Effects of Cyano Substituents on the Cope Rearrangement

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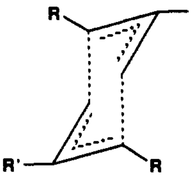
Multiconfiguration SCF (MCSCF) calculations, with the 3-21G basis set and a complete active space (CAS) wave function,[1] find the chair Cope rearrangement of 1,5-hexadiene[2] to proceed through an "aromatic" transition state (**1a**), in which bond making and bond breaking have proceeded synchronously. Although **1a** may be regarded as a resonance hybrid of two different diradical structures, **1b** and **1c**, a natural orbital analysis of the CAS-MCSCF wave function showed that the chair transition state has little diradical character.[1] In this communication we report the results of ab initio calculations on the effects of cyano groups on the transition state.

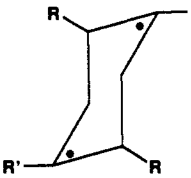
Table I. Interallylic Distances (R) and Energies (ΔE) above the Corresponding 1,5-Hexadienes for Chair Cope Transition States **1**–**3**, Calculated with the 3-21G Basis Set

transition state	R, Å SCF[b]	MP2[b]	partial CI[c]	ΔE,[a] kcal/mol SCF	FC-MP2
1	2.020	1.926	2.106	45.9[d]	28.3[e-g]
2	1.931	1.778	1.958	39.3	20.1[h]
3	2.093	2.015	2.213	44.8	26.7

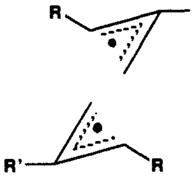
[a] Classical activation energies calculated at the SCF/3-21G geometries. Zero-point energy corrections necessary to calculate $\Delta H^{\ddagger}_0$ for **1**–**3** are, respectively, −0.2, −0.3, and −0.6 kcal/mol. [b] Full gradient optimization. [c] Optimization of only R with partial SD-CI (see text). [d] With 6-31G*, ΔE = 56.5 kcal/mol at the SCF level. [e] Using the MP2 optimized geometries for reactant and transition state, ΔE = 27.4 kcal/mol. [f] At the FC-MP4-SDTQ level, ΔE = 31.4 kcal/mol. With the 6-31G* basis set, ΔE = 31.0 kcal/mol at the FC–MP2 level and 38.7 kcal/mol at the FC-MP4-SDTQ level. [g] Experimentally, $\Delta H^{\ddagger}_{298}$ = 33.7 kcal/mol.[21] [h] Experimentally, $\Delta H^{\ddagger}_{298}$ = 23.3 kcal/mol for a monomethyl derivative.[4]



1a, R=R'=H
2a, R=H, R'=CN
3a, R=CN, R'=H



1b, R=R'=H
2b, R=H, R'=CN
3b, R=CN, R'=H



1c, R=R'=H
2c, R=H, R'=CN
3c, R=CN, R'=H

Experimental studies of the effects of cyano[3,4] and phenyl[5-7] groups have shown that both of these radical-stabilizing substituents accelerate the rate of the Cope rearrangement and are most effective when positioned at C-2 and C-5. Based on changes in the measured secondary kinetic isotope effects with substitution, Gajewski and Conrad have suggested that substituents can alter the structure of the transition state for the Cope rearrangement.[8] These authors proposed that substituents at C-2 and C-5 enhance bond making by selectively stabilizing structure **b**, relative to **c**. Similarly, substituents at C-3 and C-4 enhance bond breaking by stabilizing structure **c**, relative to **b**.[9]

In order to test the proposal of Gajewski and Conrad, we have located the transition states for the Cope rearrangement of two different dicyano-1,5-hexadienes, **2** and **3**. The transition states were located and the reactant geometries optimized by SCF calculations with the 3-21G basis set.[12] Vibrational analyses

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(9) Dewar and Jie have reported finding with AM1 that **1a** and **1b** represent two distinct transition states, whose relative energies can be altered by substituents.[10] Our attempts, with the versions of AM1 in AMPAC, MOPAC, and Gaussian 86, to find the "aromatic" C_{2h} chair transition state with R = 1.992 Å,[10] have been wholly unsuccessful and have invariably led back to the "biradicaloid" intermediate with R = 1.646 Å.[11] It should be noted that the AM1 "biradicaloid" transition states successfully reproduce the rate accelerations found experimentally[5] for phenyl substitutents at both C-2 (C-5) and C-3 (C-4).[11]

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