# A Doubly Destabilized Antiaromatic Cyclopentadienyl Cation: Solvolysis of a 5-Trifluoroacetoxy-5-heptafluoropropyl 1,3-Cyclopentadiene[1a]

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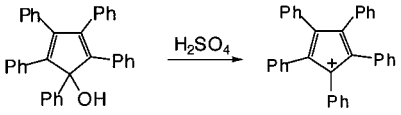
*Received June 4, 2001*

The 5-trifluoroacetoxy-5-heptafluoropropylcyclopentadiene **15** rearranges to the isomeric trifluoroacetate **16** with a rate constant $5 \times 10^5$ less than that for solvolysis of the corresponding 5-$CH_3$ derivative **5**. Labeling of **15** with $^{18}O$ shows the rearrangement occurs by a [1,5]-sigmatropic rearrangement. Solvolysis of **16** occurs at a rate 4 times slower than its formation from **15** and leads to the extensively rearranged fulvene **18**, implicating formation of the doubly destabilized cation **20**. Carbocation formation from **15** is retarded by a factor of $10^{20}$ relative to the model **11**, showing cumulative destabilizing effects due to formation of the antiaromatic cyclopentadienyl carbocation and electron withdrawal by the fluoroalkyl group.

Carbocations were first reported 100 years ago, in 1901, in independent studies by Norris,[1b,c] and by Kehrmann and Wentzel,[1d] who observed the formation of colored solutions from reaction of triphenylmethyl alcohol or chloride in concentrated $H_2SO_4$, or with $AlCl_3$ or $SnCl_4$. In 1902 Baeyer interpreted these reactions as forming salts, termed "carbonium" salts.[1e−g]

In 1925 Ziegler and Schnell[2a] reported that pentaphenylcyclopentadienol (**1**) reacted with concentrated $H_2SO_4$ with formation of a transient blue violet color (eq 1). Later studies identified the color as due to the cation **2**, which could be formed as a stable salt by treatment of **1** with $BF_3$[2b] or $SnCl_4$.[2c] This cation was found to have a low lying triplet excited state due to Jahn−Teller distortion.[2b] This history of carbocation chemistry has been summarized by Nenitzescu.[2d]




(1)

**1** **2**

The 4$\pi$-electron cyclopentadienyl cation **3**[3] and cyclopropenyl anion **4**[4] are the prototypes of antiaromatic ions. The singlet cation is calculated to be destabilized by 42.0 kcal/mol relative to the pentadienyl cation,[3d] and this destabilization is manifested by the estimated p$K_R^+$ of −40 or less for this species.[3a] Despite this great destabilization, the cation has been observed by electron spin resonance in a matrix, and the spectrum confirms the triplet nature of the cation.[3b] The cyclopropenyl anion **4** has never been observed and from calculations is strongly pyramidalized and would spontaneously lose an electron to form the cyclopropenyl radical in the gas phase.[4c] The planar conjugated form is calculated not to be an energy minimum structure.


**3** **4**

In 1997 we reported the first kinetic studies of the generation of a cyclopentadienyl cation, namely the reaction of **5** forming **6** (Scheme 1).[3c] In $CF_3CH_2OH$ (TFE), solvolysis led to the products **7**−**10**, and the variation of the rate constants log *k* for **5** in different solvents gave a dependence *m* on the solvent parameters for ionization of trifluoroacetate $Y_{OTFA}$ of 0.97. The diverse group of products formed and the strong dependence of the reactivity on the solvent ionizing power both gave convincing evidence for the formation of the cation **6**.

The rate constant for solvolysis of the cyclopentenyl trifluoroacetate **11** forming **12** was estimated to exceed that of **5** forming **6** by a factor of $10^{14}$, and the enormous rate retardation due to the additional double bond in **5** was attributed to antiaromatic destabilization in the 4$\pi e^-$ anti-Hückel system. The large magnitude of this destabilization is consistent with the evidence for antiaroma-

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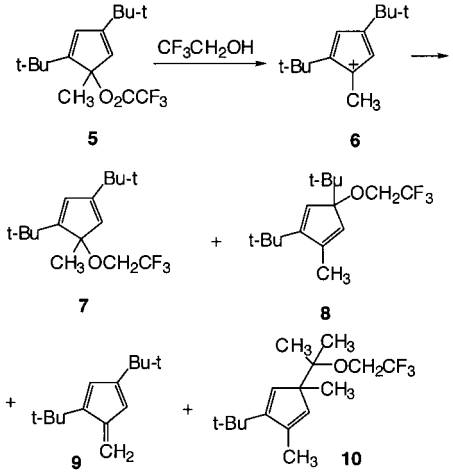
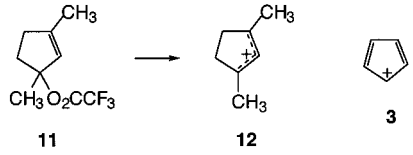
10.1021/jo010562g CCC: $20.00 
Published on Web 10/24/2001

**Scheme 1**



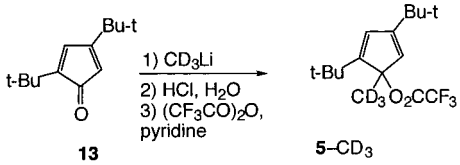

ticity in the parent cyclopentadienyl cation **3** including the electrochemical studies,[3a] the calculated 42.0 kcal/mol destabilization relative to the pentadienyl cation,[3d] the nucleus independent chemical shift (NICS), and the IGLO calculated magnetic susceptibility exaltation $\lambda_{tot}$.[3d]




Because of the unique nature of the cation **6**, it appeared desirable to examine further mechanistic criteria for formation of this ion. In particular, the secondary isotope effect $k(CH_3)/k(CD_3)$ is a useful diagnostic tool for the elucidation of the nature of carbocations, with smaller values for rather stabilized carbocations, and larger values for less stable cations with higher electron demand. Also electron-withdrawing substituents provide an alternative means for destabilizing carbocations,[5] and it is of interest to test for the effect of such a substituent in conjunction with this antiaromatic system. Previously we have determined rate ratios for the substituents $H/CF_3$ for the indenyl[5g] and fluorenyl carbocations[5h] of $10^3$ in both cases, but the cyclopentadienyl system is much more destabilized, and the fluoroalkyl substituent would be compared to $CH_3$. However, despite the greatly depressed reactivity of **5** compared to **11**, it is nevertheless notable that a rate constant for **5** could still be measured in hexafluoro-2-propanol (HFIP) at 25 °C,[3c] and this suggested that such a doubly destabilized carbocation might be experimentally accessible.

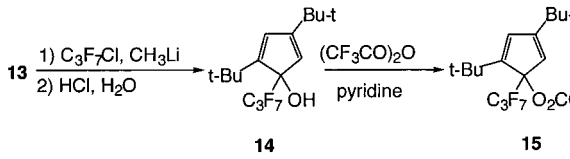
## Results and Discussion

To measure the isotope effect on the reaction of **5** the analogue **5**-$CD_3$ was prepared by reaction of the ketone **13** with $CD_3Li$ followed by treatment with trifluoroacetic anhydride and pyridine (eq 2), by analogy to the preparation of **5**. The measured solvolysis rate constant for **5**-$CD_3$ in 97% hexafluoro-2-propanol (HFIP) at 25 °C was $1.18 \times 10^{-3}$ s$^{-1}$ and shows an isotope effect $k(CH_3)/k(CD_3)$ of $1.30 \pm 0.06$, which is comparable to that of 1.33 found for PhCOTs($CF_3$)Me.[5a] Thus, this criterion provides further evidence for the formation of the highly destabilized cation **6** with strong electron demand.




(2)

To test whether an even more destabilized carbocation could be generated we chose a fluoroalkyl-substituted analogue of **5**, as the destabilizing effects of $CF_3$ and $C_2F_5$ groups have been repeatedly demonstrated.[5] Treatment of ketone **13** with $CF_3SiMe_3$[6] using KF/*t*-BuOK or TBAF in THF gave no reaction in either case, but reaction of **13** with $CF_3CF_2CF_2I$ and $CH_3Li$ gave the alcohol **14**, which was converted to the trifluoroacetate **15** on treatment with trifluoroacetic anhydride and pyridine (eq 3).




(3)

Upon heating of **15** in TFE-$d_3$ at 100 °C with measurement of the product composition at intervals by $^1$H NMR, the disappearance of **15** occurred with a rate constant estimated as $1.5 \times 10^{-5}$ s$^{-1}$, with predominant conversion back to the alcohol **14**, along with formation of about 10% of a rearranged product assigned to the structure **16** (vide infra), with $k$ of $1.8 \times 10^{-6}$ s$^{-1}$. The formation of **14** is indicative of nucleophilic attack by TFE at the carbonyl carbon with acyl−oxygen cleavage. In HFIP at 100 °C conversion to **16** is more efficient, to the extent of 25% after 21 h. However, isolated **16** reacts further to give fulvene **18** as the major product, with a **16**/**18** ratio of 79/21 after 57.5 h, with an estimated rate constant of $1.1 \times 10^{-6}$ s$^{-1}$ at 100 °C. Beginning with **15** in HFIP, the product after 67 h was determined by $^1$H NMR to contain **14**, **15**, **16**, and **18** in a ratio of 9, 37, 43, and 11, respectively. Extensive NMR study of the isomeric trifluoroacetate, especially the NOE enhancement (see Supporting Information), favors the structure **16** in preference to the alternative structure **17** (eq 4).

Measurement of the kinetics of the isomerization of **15** by $^1$H NMR in $(CF_3)_2CDOD$ gave a rate constant of 3.7 $\times 10^{-6}$ s$^{-1}$ at 100 °C, and a rate constant for the reaction of **5** in HFIP at 100 °C was calculated as 1.9 s$^{-1}$ from the extrapolated rate constant of **5** in TFE at 100 °C of 4.5 $\times 10^{-2}$ s$^{-1}$ and the HFIP/TFE rate ratio for **5** at 25 °C of

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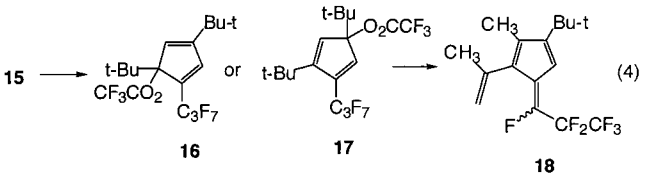
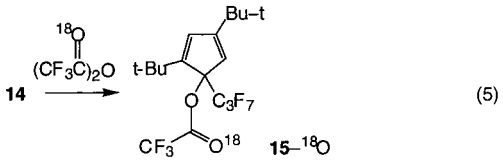



(4)

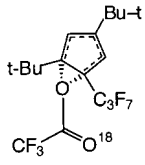
42.[3c] Thus, the solvolysis rate constant of **5** in HFIP at 100 °C is greater than the rate of rearrangement of **15** by a factor of $5 \times 10^5$ and exceeds the rate constant for solvolysis of **16** by a factor of $2 \times 10^6$.

Two possible pathways for the rearrangement of **15** forming **16** may be envisaged. One is formation of a carbocation/trifluoroacetate ion pair, and a second is an electrocyclic rearrangement. To differentiate these possibilities, the carbonyl $^{18}O$ labeled derivative **15**-$^{18}O$ was prepared by the reaction of **14** with $^{18}O$ labeled $(CF_3CO)_2O$ (eq 5).[7a,b] The $^{18}O$ content in **15**-$^{18}O$ was determined by the $^{18}O$-induced isotope shift of the $^{13}C$ NMR of the carbonyl carbon as done previously[5b] as 24 ± 4% in the carbonyl oxygen and none in the alkyl C−O.




(5)

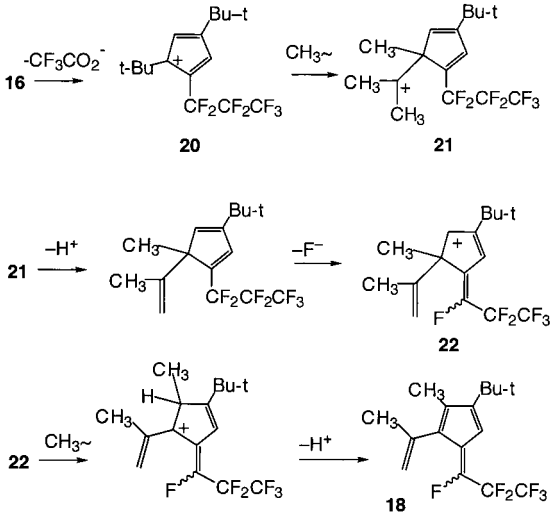
The sample of **15**-$^{18}O$ was heated at 100 °C in HFIP, the product mixture was separated, and the $^{18}O$ distribution as determined from the $^{13}C$ NMR spectrum for **16** was 24 ± 4% in the carbonyl oxygen, and 0 ± 4% in the alkyl C−O, while recovered **15**-$^{18}O$ showed the same $^{18}O$ distribution as in the starting material. The $^{18}O$ distribution in **15** and **16** was also determined from their IR spectra, as recovered **15**-$^{18}O$ showed bands at 1800 and 1765 $cm^{-1}$ due to C=$^{16}O$ and C=$^{18}O$ in a 77/23 integrated ratio, respectively, and the rearranged **16**-$^{18}O$ showed absorptions at 1793 and 1758 $cm^{-1}$, in a 76/24 ratio. Isotopic shifts of 25−30 $cm^{-1}$ to lower frequency upon $^{18}O$ substitution were reported for a variety of aldehydes and ketones.[7c] Thus, within the limits of detectability, the rearrangement occurred exclusively with migration of the O originally bonded to the cyclopentadienyl moiety, and the reaction may be represented as a [1,5]-sigmatropic rearrangement through the transition state **19**.




**19**

The occurrence of the rearrangement by a [1,5]-sigmatropic shift also provides further evidence against the structure **17**, as this could only be formed by a series of such processes and would lead through a secondary trifluoroacetate expected to be less reactive than either **16** or **17**. Rearrangements of trifluoroacetoxy groups in penta(aryl)cyclopentadienyl systems have been observed before and were proposed to occur by [3.3]-sigmatropic pathways,[8a] in contrast to the results found here. The [3,3]-sigmatropic pathway was favored over the [1,5]-pathway by analogy to another study of the rearrangement of an amidinyl species using NMR identification of the aryl groups.[8b] However a [1,5]-pathway was favored for the migration of arylthio groups in methyl(tetramethoxycarbonyl)cyclopentadienes.[8c] [1,5]-Rearrangements are well documented in cyclopentadienyl derivatives.[8d−f]

**Scheme 2**




The preference for the formation of the product **16** as opposed to **17** is in contrast to the formation of **8** from **5**, but is consistent with the different mechanistic pathways followed. Reaction of **15** by the [1,5]-sigmatropic pathway leads to **16**, while **8** is formed by capture of the intermediate carbocation **6** by solvent. Approximate rate constants for the [1,5] rearrangement in TFE and HFIP were estimated above as 1.8 and 3.7 ($\times 10^{-6}$ $s^{-1}$), respectively. Based on the solvent ionizing power parameters $Y_{OTFA}$ of 2.25 and 3.37, respectively,[3c] for these solvents the calculated substrate dependence *m* on solvent ionizing power is 0.3, and this low value is consistent with the rather nonpolar transition state **19**.

The formation of the extensively rearranged fulvene **18** on further reaction of **16** provides strong evidence the carbocation **20** is formed, and a possible pathway for the formation of **18** is shown in Scheme 2. This involves initial methyl migration forming **21** followed by proton loss and then ionization of fluoride to give cation **22**, which after methyl rearrangement and proton loss gives **18**. Loss of fluoride from perfluoroalkyl groups under ionizing conditions is well-known.[5i]

In conclusion reaction of **15** by [1,5] sigmatropic rearrangement to **16** followed by formation of the doubly destabilized carbocation **20** has been demonstrated.

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There is a rate retardation for ionization of **16** relative to the model **11** by a factor of $10^{20}$. A cumulative effect of the destabilization due to the antiaromaticity of the cyclopentadienyl cation and the electron withdrawal by the perfluoropropyl group is observed.

## Experimental Section

Glassware was flame dried, and reactions were conducted in an atmosphere of nitrogen or argon. Chromatography was carried out using hexane and silica gel. Kinetic measurements were carried out as described previously.[3c]

**Preparation of 5-$CD_3$.** Addition of $CD_3Li$ was carried out as for $CH_3Li$,[3c] and the resulting alcohol was reacted with $(CF_3CO)_2O$ and pyridine as before[3c] to give **5**-$CD_3$. $^1$H NMR ($CDCl_3$) $\delta$ 1.10 (s, 9), 1.22 (s, 9), 5.75 (d, 1, $J$ = 2.1 Hz), 6.06 (d, 1, $J$ = 2.1 Hz). $^{13}$C NMR ($CDCl_3$) 21.0 (septet, $J_{CD}$ = 19.3 Hz), 28.5, 30.5, 31.9, 34.1, 95.3, 114.4 (q, $J_{CF}$ = 287 Hz), 124.6, 126.6, 155.0, 155.6 (q, $J_{CF}$ = 41.6 Hz), 157.0. $^{19}$F NMR ($CDCl_3$) $\delta$ −75.8 (s). HREIMS $m/z$ calcd for $C_{16}H_{20}D_3F_3O_2$ 307.1838, found 307.1832.

**Kinetics of 5-$CD_3$.** Solvolysis rates for **5** and **5**-$CD_3$ in 97% HFIP with 2 equiv of 2,6-lutidine at 25 °C were measured as previously[3c] by observing the decrease in the UV absorption at 280 nm and gave rate constants of $(1.54 \pm 0.08) \times 10^{-3}$ s$^{-1}$ and $(1.18 \pm 0.07) \times 10^{-3}$ s$^{-1}$, respectively.

**Preparation of 14.** To a solution of ketone **13**[3c] (76 mg, 0.39 mmol) in 5 mL of ether cooled to −78 °C and $n$-$C_3F_7I$ (86 $\mu$L, 0.59 mmol) was added slowly 1.5 M MeLi in ether (0.36 mL, 0.54 mmol), and the solution was stirred 30 min, warmed, acidified, and extracted with ether. The solution was dried, concentrated, and chromatographed giving **14** (33 mg, 24%). $^1$H NMR ($CDCl_3$) $\delta$ 1.11 (s, 9), 1.26 (s, 9), 2.37 (s, 1), 5.58 (m, 1,), 6.21 (d, 1 $J$ = 1.8 Hz). $^{13}$C NMR ($CDCl_3$) 28.4, 31.0 (t, $J_{CF}$ = 2.3 Hz), 32.4, 34.6, 88.4 (dd, $J_{CF}$ = 27.4, 20.9 Hz), 108−120 (m, 3, split by F), 121.7−121.8 (m, 1), 131.0, 157.4, 159.0. $^{19}$F NMR ($CDCl_3$) $\delta$ −81.3 (t, 3, $J$ = 10.5 Hz), −111.6 (octet of d, 1, $J$ = 282 Hz), −116.4 (sextet of d, 1, $J$ = 282 Hz), −123.8 (m, 2). EIMS $m/z$ 362 (26), 347 (28), 319 (68), 305 (22), 289 (23), 193 (25), 57 (100). HREIMS $m/z$ calcd for $C_{16}H_{21}F_7O$ calcd 362.1481, found 362.1490.

**Preparation of 15.** A solution of **14** (29 mg, 0.080 mmol), pyridine (50 $\mu$L, 0.62 mmol), and $(CF_3CO)_2O$ (40 $\mu$L, 0.28 mmol) was stirred 1 h at 25 °C. Then ether and ice−$H_2O$ were added, and the ether layer was washed with $NaHCO_3$, dried, evaporated, and chromatographed (hexane) to give **15** (12 mg, 0.026 mmol, 33%): $^1$H NMR ($CDCl_3$) $\delta$ 1.13 (s, 9), 1.20 (s, 9), 5.51 (ddd, 1, $J$ = 5.2, 3.3, 1.9 Hz), 6.46 (d, 1, $J$ = 1.8 Hz). $^{13}$C NMR ($CDCl_3$) 28.2, 30.6, 32.7, 34.6, 93.9 (dd, $^2J_{CF}$ = 32.7, 21.2 Hz), 109−119 (m, split by F), 113.9 (q, $^1J_{CF}$ = 286 Hz), 116.2, 134.8, 152.2, 153.0 (q, $^2J_{CF}$ = 43.3 Hz), 161.6. $^{19}$F NMR ($CDCl_3$) $\delta$ −75.6 (s, 3), −81.2 (dd, 3, $J$ = 12.6, 8.8 Hz), −110.1 (quintet of d, 1, $J$ = 278 Hz), −119.7 (sextet of d, 1, $J$ = 278 Hz), −123 (m, 2). IR ($CDCl_3$) 1801 cm$^{-1}$. EIMS $m/z$ 458 (0.3), 155 (19), 57 (100). HREIMS $m/z$ calcd for $C_{18}H_{20}F_{10}O_2$ calcd 458.1304, found 458.1308.

**Solvolysis of 15.** A solution of **15** (31 mg, 0.067 mmol) and 2,6-lutidine (10 $\mu$L, 0.086 mmol) in 0.5 mL of HFIP in a sealed tube was heated 66.7 h in a boiling water bath. The solvent was evaporated and examination by $^1$H NMR gave the ratio of **14**, **15**, **16**, and **18** as 9, 37, 43, and 11, respectively. The solvent was evaporated and chromatography on silica gel (hexane) gave **16** as a yellow oil (9 mg, 29%): $^1$H NMR ($CDCl_3$) $\delta$ 1.13 (d, 9, $J$ = 0.9 Hz), 1.15 (s, 9), 5.91 (t, 1, $J$ = 2.0 Hz), 7.02 (m, 1). $^{13}$C NMR ($CDCl_3$) $\delta$ 26.8 (t, $J_{CF}$ = 2.4 Hz), 28.5, 32.4, 38.5 (d, $J_{CF}$ = 0.7 Hz), 100.8, 109−119 (m), 114.2 (q, $J_{CF}$ = 287 Hz), 130.2 (d, $J_{CF}$ = 3.7 Hz), 132.4 (dd, $J$ = 29.0, 19.6 Hz), 142.4 (m), 154.4 (q, $J_{CF}$ = 42.3 Hz), 155.2. $^{19}$F NMR ($CDCl_3$) $\delta$ −75.7 (s, 3), −80.3 (dd, 3, $J$ = 13.0, 10.7 Hz), −96.9 (md, 1, $J$ = 291 Hz), −111.3 (md, 1, $J$ = 296 Hz), −124 (m, 2). IR ($CDCl_3$) 1792 cm$^{-1}$. EIMS 458 (0.1), 57 (100). HREIMS $m/z$ calcd for $C_{18}H_{20}F_{10}O_2$ calcd 458.1304, found 458.1312. Structure established by ROESY, HSQC, CIGAR.

A solution of **15** (5 mg, 0.011 mmol) in TFE-$d_3$ (1 mL) containing 2 $\mu$L (0.017 mmol) of 2,6-lutidine was sealed in an NMR tube and heated in a boiling water bath, and the $^1$H NMR was measured at intervals, giving an estimated rate constant of $1.5 \times 10^{-5}$ s$^{-1}$ for disappearance of **15**. After 73 h the product consisted of **14**, **15**, and **16** in a ratio of 82, 8, 10, and $k$ for formation of **16** is estimated as $1.8 \times 10^{-6}$ s$^{-1}$.

**Solvolysis of 16.** A solution of **16** (23 mg, 0.051 mmol) and 2,6-lutidine (7 mg, 0.066 mmol) in 0.6 mL of HFIP in a sealed tube was heated 57.5 h in a boiling water bath. The solvent was evaporated and the $^1$H NMR spectrum showed the presence of **18** and unreacted **16** in a 21/79 ratio, respectively, corresponding to $k$ of $1.1 \times 10^{-6}$ s$^{-1}$ for the conversion of **16** to **18**. Chromatography on silica gel (hexane) gave **18** as a yellow oil: $^1$H NMR ($CDCl_3$) $\delta$ 1.20 (s, 9), 1.93 (q, 3, $J$ = 1.5, 1.0 Hz), 2.00 (d, 3, $J$ = 3.8 Hz), 4.89 (q, 1, $J$ = 2.1, 1.0 Hz), 5.28 (t, 1, $J$ = 1.8 Hz), 5.99 (bs, 1). $^{13}$C NMR ($CDCl_3$) $\delta$ 13.2 (d, $J_{CF}$ = 2.4 Hz), 13.3 (d, $J_{CF}$ = 2.3 Hz), 24.7, 29.8, 34.3, 68.2, 111.5, 117.5, 128.0, 131.4 (d, $J_{CF}$ = 8.3 Hz), 141.8, 144.1(td, $J_{CF}$ = 277, 29.4 Hz), 148.6, 161.1 (d, $J_{CF}$ = 8.0 Hz). $^{19}$F NMR ($CDCl_3$) $\delta$ −84.0 (ddd, 3, $J$ = 6.1, 3.0 Hz), −116.7 (dq, 2, $J$ = 3.1 Hz), −119.1 (1, bs). UV $\lambda_{max}$ (hexane) 250 ($\epsilon$ 15 000), 390 ($\epsilon$ = 150). EIMS 324 (61), 309 (100), 205 (72). Structure established by COSY, HSQC, CIGAR.

**Kinetic Measurements.** A solution of **15** (7.4 mg, 0.016 mmol) in 1 mL of HFIP-$d_2$ and 2,6-lutidine (2.2 $\mu$L, 0.02 mmol) with a $C_6D_6$ insert was sealed in an NMR tube and heated in a boiling water bath. The tube was removed at intervals, and the $^1$H NMR spectrum was integrated, giving a rate constant for disappearance of **15** of $3.7 \times 10^{-6}$ s$^{-1}$.

**Preparation of 15-$^{18}$O.** [7a,b] Trifluoroacetyl chloride (5 g, 40 mmol) was condensed onto $H_2O$−97% $^{18}$O (0.1 g, 5 mmol) cooled at −78 °C, and the solution was warmed to room temperature, giving 230 $\mu$L of crude $CF_3CO_2H$, which was added to a flask containing $P_2O_5$ (0.48 g, 1.7 mmol). The system was closed with a septum, the mixture was heated 1 h at 80 °C, and then the volatile material was collected in a receiver cooled to −78 °C by heating to 100 °C under argon. The mixture was warmed to room temperature, **14** (86 mg, 0.024 mmol) in 100 $\mu$L of pyridine was added, and the solution was stirred 30 min. The product was dissolved in hexane which was evaporated, and chromatography gave **15**-$^{18}$O (33 mg, 0.072 mmol), pure by NMR. The C=$^{18}$O content was determined as 24 ± 4% from integration of the $^{13}$C NMR spectrum, in which the carbonyl $^{13}$C bonded to $^{18}$O was shifted by 0.033 ppm upfield, and no incorporation in the alkyl C−O was detected.

**Rearrangement of 15-$^{18}$O.** The **15**-$^{18}$O (33 mg, 0.072 mmol) in 0.7 mL of HFIP and 11 $\mu$L (0.093 mmol) of 2,6-lutidine was sealed in a tube and heated 68 h at 100 °C. The solvent was evaporated and the $^1$H NMR spectrum showed the presence of **14**, **15**, **16**, and **18** in a ratio of 3, 40, 48, and 9, respectively. Chromatography (hexane) gave **15** (7 mg, 21%) and **16** (15 mg, 45%). Analysis of the $^{18}$O content of recovered **15** was determined as 24 ± 4% in the carbonyl oxygen by integration of the $^{13}$C NMR spectrum of C=$^{18}$O 0.033 ppm upfield from C=$^{16}$O, and 23 ± 4% in the carbonyl oxygen with 0 ± 4% for the alkyl-O in **16**. The IR spectrum of **15** showed bands at 1800 and 1765 cm$^{-1}$ assigned to C=$^{16}$O and C=$^{18}$O in a 77/23 integrated ratio, respectively, and **16** showed bands at 1793 and 1758 cm$^{-1}$ assigned to C=$^{16}$O and C=$^{18}$O, respectively, in a 76/24 ratio.

**Acknowledgment.** Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

**Supporting Information Available:** $^1$H and 2D NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010562G