Solvolytic Generation of Antiaromatic Cyclopentadienyl Cations

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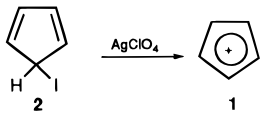
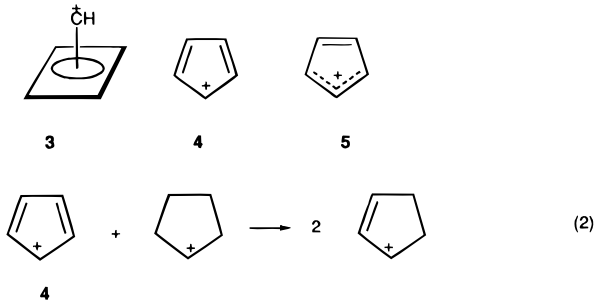
Abstract: Solvolysis of 1,3-di-*tert*-butyl-5-methyl-5-cyclopenta-1,3-dienyl trifluoroacetate (**15a**) occurs with a strong dependence on solvent ionizing power ($m = 0.97$), and gives products of substitution, allylic and skeletal rearrangement with substitution, and elimination. These results are characteristic of a process involving an intermediate carbocation, and provide the first measurements of the kinetics of formation of a cyclopentadienyl cation, the prototypical 4π-electron carbocation destabilized by antiaromaticity. The reactivity of **15a** in 2,2,2-trifluoroethanol at 25 °C is calculated to be lower than those of analogous fluorenyl and indenyl derivatives by factors of 3×10^4 and 4×10^2, and is exceeded by that calculated for 1,3-dimethyl-3-cyclopentenyl trifluoroacetate by a factor of 10^{14}, showing the large carbocation destabilizing effects of antiaromaticity.

The cyclopentadienyl cation (**1**) is the prototypical carbocation destabilized by 4π-electron antiaromaticity,[1] and has long been the subject of study.[2,3] These investigations include the electrochemical determination of the pK_R^+ as −40 or lower, which is 20 units lower than those for representative conjugated cations,[2c] observation of $C_5H_5^+$ as a triplet with the D_{5h} structure **1** in a matrix of SbF_5 at 78 K,[2d] and the failure of cyclopentadienyl iodide to form $C_5H_5^+$ solvolytically even when treated with silver perchlorate in propionic acid at −15 °C (eq 1).[2b] By contrast **2** is 10 times more reactive than cyclopentyl iodide in bimolecular reaction with bromide.[2e]



2 **1** (1)

Carbon scrambling of $C_5H_5^+$ in the gas phase is suggested to involve pyramidal ions **3**,[2f] although the singlet ion is calculated[3c] to prefer C_{2v} ethylene-type structures **4** which interconvert with an extemely low 0.09 kcal/mol barrier through C_{2v} allylic-type structures **5**. The calculated[3d] magnetic susceptibility exaltation and the homodesmotic destabilization of **4** of 56.7 kcal/mol for the reaction of eq 2 both indicate major antiaromaticity effects.



4 (2)

These studies indicate that cyclopentadienyl carbocations are highly destabilized and that their generation under solvolytic conditions might be considered unattainable, but there are some recent indications that such species may indeed be generated in solution. Thus, the reaction of pentamethylcyclopentadienyl bromide (**6**) with silver tetrafluoroborate at −10 °C in CH_2Cl_2 with methanol, methylamine, dimethylamine, pyridine, and dimethyl sulfide led to substitution products, which could result by capture of the pentamethylcyclopentadienyl cation (**7**) by the nucleophiles (eq 3).[4a] Also the reaction of 5-tolyl-1,2,3,4-tetraphenylcyclopentadienyl bromide (**8**) with substituted silver acetates gave a nonequilibrium mixture of acetate esters **10**, presumably through the cation **9** (eq 4).[4b] Upon heating in the range of 50−150 °C the acetates **10** underwent equilibration in a process which was catalyzed by Hg(II) and Pd(II) salts, and this transformation was ascribed to 3,3-sigmatropic rearrangements of the acyloxy groups.[4b]

Despite these extensive previous studies of cyclopentadienyl cations, and speculations "that rate-accelerating substituent effects may be used for increasing the reactivity of cyclopentadienyl precursors into an experimentally convenient range",[4c] there have been no reported measurements of the kinetics of the solvolytic reactivity of cyclopentadienyl derivatives leading to cyclopentadienyl cations. We have been engaged in the study

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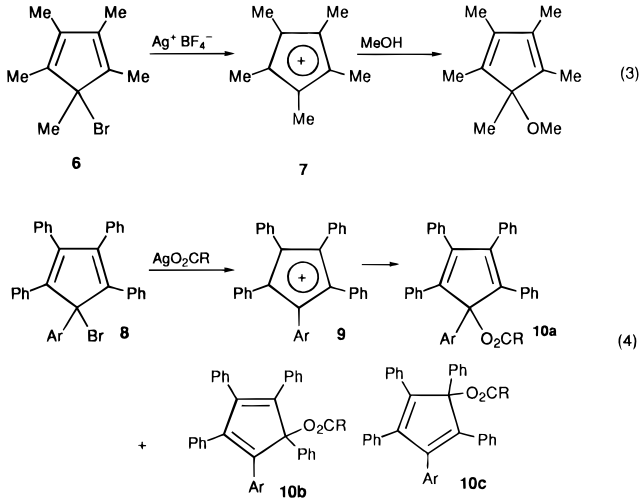
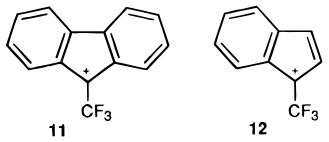
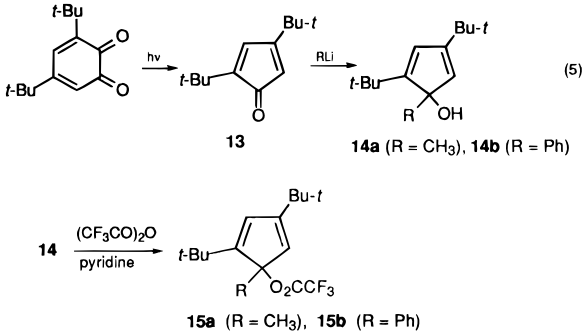


of the solvolytic generation of CF_3-substituted doubly-destabilized fluorenyl (**11**)[5a] and (**12**)[5b] indenyl carbocations, and other destabilized carbocations,[5c,d] and now report the first kinetic studies of cyclopentadienyl cation formation.



Results

Photolysis of commercially available 3,5-di-*tert*-butyl-*o*-benzoquinone gives efficient formation of 2,4-di-*tert*-butylcyclopentadienone (**13**),[6] which on reaction with methyllithium or phenyllithium forms the alcohols **14a** and **14b**, respectively, which are converted by trifluoroacetic anhydride to the respective trifluoroacetates **15** (eq 5). Trifluoroacetate leaving groups



have been frequently exploited in studies of solvolysis.[7] They are easy to prepare even for crowded substrates, and have a convenient reactivity intermediate between those of tosylate and *p*-nitrobenzoate leaving groups.[7] The substrates **14** and **15** showed no evidence for dimerization by [4 + 2] cycloaddition under the conditions of these experiments, and this is due to the presence of the bulky *tert*-butyl groups.[6c]

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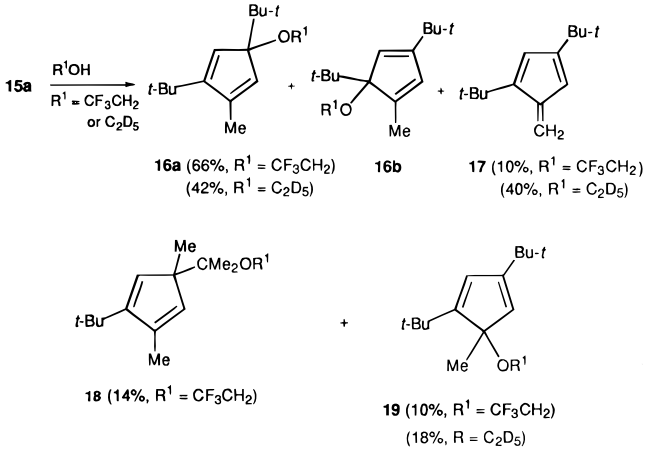
Table 1. Solvolytic Rate Constants[a] for 5-Methyl- and 5-Phenyl-1,3-di-*tert*-butyl-5-cyclopenta-1,3-dienyl Trifluoroacetate (**15a,b**)

			k_{obsd} ($s^{-1} \times 10^4$)		
solvent	Y_{OTFA}	T (°C)	5-Me (**15a**)	5-Ph (**15b**)	k_{Me}/k_{Ph}
97 HFIP	3.37 (3.61)[b]	25	15.4	3.67	4.2
97 HFIP[c]		25	14.4		
97 TFE[c]	2.25 (1.83)[b]	70.1	36.5	15.8	2.3
		54.4	8.68	4.23	2.1
		43.6	2.72	0.928	2.9
		25[d,f]	0.343	0.138[e]	2.5
80 EtOH[c]	0.0	76.0	1.76		
		64.8	0.453		
		54.8	0.204		
		25.0[d,g]	0.00543		
60 MeOH[c]	1.50	62.6	9.16		
	(1.52)[b]	53.9	3.82		
		44.2	1.25		
		25.0[d,h]	0.124		
80 MeOH[c]	0.63 (0.47)[b]	62.7	1.81		
		53.9	0.625		
		44.3	0.249		
		25.0[d,i]	0.023		

[a] Duplicate runs at each temperature, ±3%. [b] Y_{OTs}. [c] Containing 2 equiv of 2,6-lutidine. [d] Extrapolated from data at higher temperatures. [e] $\Delta H^{\ddagger} = 20.9$ kcal/mol, $\Delta S^{\ddagger} = -10.8$ cal mol^{-1} K^{-1}, log $k = 1.28$ $Y_{OTFA} - 7.74$. [f] $\Delta H^{\ddagger} = 20.5$ kcal/mol, $\Delta S^{\ddagger} = -10.3$ cal mol^{-1} K^{-1}, log $k = (0.97 \pm 0.09)$ $Y_{OTFA} - (6.33 \pm 0.17)$. [g] $\Delta H^{\ddagger} = 22.5$ kcal/mol, $\Delta S^{\ddagger} = -11.8$ cal mol^{-1} K^{-1}. [h] $\Delta H^{\ddagger} = 22.3$ kcal/mol, $\Delta S^{\ddagger} = -6.2$ cal mol^{-1} K^{-1}. [i] $\Delta H^{\ddagger} = 22.1$ kcal/mol, $\Delta S^{\ddagger} = 10.1$ cal mol^{-1} K^{-1}.

Scheme 1



The reactions of **15a** and **15b** in 97% 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and 97% 2,2,2-trifluoroethanol (TFE), and of **15a** in 60% MeOH, 80% MeOH, and 80% EtOH, were monitored by UV spectroscopy and took place with first-order kinetics, as reported in Table 1. The rates of these reactions gave correlations with the solvent parameters for trifluoroacetate leaving groups Y_{OTFA}[7c,d] by the relationships log $k = (0.97 \pm 0.09)Y_{OTFA} - (6.33 \pm 0.17)$ for **15a** and log $k = 1.28Y_{OTFA} - 7.74$ for **15b**. The Y_{OTFA} values[7c,d] for these solvents are rather similar to the corresponding Y_{OTs} values, as noted in Table 1. For **15a** the use of Y_{OTs} values gives the correlation log $k = (0.93 \pm 0.04)Y_{OTs} - (6.20 \pm 0.08)$.

Preparative scale solvolysis of **15a** in CF_3CH_2OH and chromatographic separation of the products led to the isolation of **16a, 17, 18**, and **19** (Scheme 1), whose structures were established by their spectroscopic properties as described below. On the basis of integration of the ^{1}H NMR signals for the crude reaction mixture the relative yields of **16**−**19** ($R^1 = CF_3CH_2$)

were 66, 10, 14, and 10%, respectively. To estimate the comparative yields for solvolysis in C_2D_5OD, the product of a small-scale run was analyzed by ^{1}H NMR as containing **16a**, **17**, and **19** ($R^1 = C_2D_5$) in relative percentages of 42, 40, and 18. Structures were assigned from the ^{1}H NMR signals corresponding to products identified in the study in CF_3CH_2-OH. The products in C_2D_5OD were also analyzed by GC/MS and assigned by the EIMS fragmentation patterns, and the possible presence of the isomeric structure **16b** was also noticed. Determinations of the relative yields (parentheses) of products for $R^1 = C_2D_5$ from the GC peak areas were **16a** (43), **16b** (3), **17** (32), **18** (<1), and **19** (17%), with 5% starting material, and these are in reasonable agreement with the independent measurement by ^{1}H NMR. Thus, although the products for the reaction in C_2D_5OD were not isolated and positively identified, there are indications that the pattern of products in this medium is similar to that in TFE.

The identification of the unrearranged substitution product **19**−OCH_2CF_3 follows from the close resemblance of the ^{1}H and ^{13}C NMR spectra to those of **14a** and **15a**, including the ^{1}H NMR absorption of the carbinyl methyl at δ 1.55 and the 2,4-vinyl hydrogens at δ 6.05 and 5.35, respectively, as compared to values of 1.53, 5.87, and 5.48, respectively, for **14a**, and 1.74, 6.06, and 5.75 for **15a**. This compound also showed a distinct nonequivalence of the diastereotopic CH_2 protons of the CH_2CF_3 group, with the absorption of the protons as two overlapping quartets at δ 3.503 and 3.513 ($J_{H,F} = 8.9$ Hz). The structure of the product of allylic rearrangement **16a** was assigned as a cyclopentadiene on the basis of its UV λ_{max}^{hexane} of 271 nm, as compared to values of 280 and 277 nm, respectively, for **14a** and **15a**, and the ^{1}H NMR absorptions for the vinyl CH_3 and the 1,4-vinyl hydrogens at δ 2.07, 5.64, and 5.70, respectively, which are distinctly different from the pattern for the 1,3-disubstituted cyclopentadienes **14a** and **15a**. The vinyl proton at δ 5.64 shows a 2.6 Hz coupling to the other vinyl proton, and the latter also shows coupling to the vinyl CH_3. The diastereotopic CH_2 protons of the CH_2CF_3 group differ in chemical shift by only δ 0.003, and this small difference is consistent with this structure, as opposed to an isomeric structure resembling **16b**, as the different alkyl groups in **16a** which render these protons nonequivalent are rather remote. The fulvene structure of **17**, which is bright yellow in color, follows from the UV $\lambda_{max}^{hexane} = 246$ ($\epsilon = 15\,000$) and 370 ($\epsilon = 420$) nm, which resembles the published UV spectrum of the parent,[8] and also from the other consistent spectral data, including assignment of the vinyl protons from a ^{1}H−^{13}C heteronuclear correlated spectrum.

Compounds **14a**, **15a**, and **19** all show two vinyl *tert*-butyl groups, one between δ 1.08 and δ 1.10, and one between δ 1.21 and δ 1.24, in the ^{1}H NMR. Therefore, in **16a** the vinyl *tert*-butyl at C-2 is that at δ 1.19, and the carbinyl *tert*-butyl at C-5 is that of δ 0.97.

The structure of the Wagner−Meerwein rearranged product **18** follows from the ^{1}H NMR signals for the carbinyl methyl, geminal methyls, vinyl methyl, and 1,4-dienyl protons at δ 1.106, 1.114, 2.05, 5.87, and 5.92, respectively, and the consistent ^{13}C NMR signals. The vinyl methyl and 1,4-dienyl proton signals are similar to those of **16a**, and quite different from those of the 1,3-disubstituted derivatives **14a** and **15a**, which show the vinyl CH_3 at higher field, and a significantly greater spacing between the vinyl protons. The UV $\lambda_{max}^{hexane} = 246$ ($\epsilon = 2000$) is somewhat shifted from those of **14a**, **15a**, **16a**, and **19**, perhaps because of the different substitution pattern at C-5. The absence of visible nonequivalence of the diastereotopic geminal methyl groups or of the CH_2 protons of the CH_2CF_3 group is also consistent with this structure as opposed to an isomeric 1-methyl-3-*tert*-butyl structure, in which there would be a greater probability of observable nonequivalence because of the proximity of the CH_3 at C-1.

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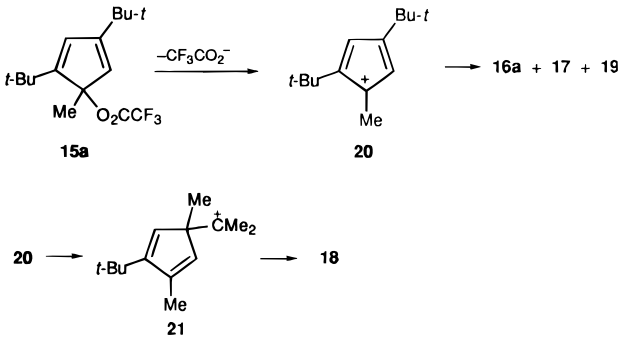
Scheme 2



Discussion

The kinetic data for both substrates **15a** and **15b** show a strong dependence on solvent polarity, with 3000-fold greater reactivity for **15a** in 97% HFIP compared to 80% EtOH at 25 °C, and *m* values of 0.97 and 1.28, respectively. These large values are diagnostic that the reactions occur by carbocationic processes. This conclusion is consistent with the finding that the reaction products from **15a** in TFE and EtOH represent elimination, substitution, substitution with allylic rearrangement, and substitution with skeletal rearrangement. Such a mixture of products is characteristic of a carbocationic process.

A noticeable feature of the rate data is that the phenyl-substituted derivative **15b** is less reactive than the methyl compound **15a**, by factors of 2.1−4.2 (Table 1). This is contrary to the behavior observed in unhindered systems, where phenyl groups accelerate carbocationic reactivity by significant factors compared to methyl, but is typical of crowded compounds, where the phenyl is twisted out of conjugation, and destabilizes the developing carbocationic center due to inductive effects.[9] Thus, for compounds RR'_2COPNB in 70% acetone at 100 °C the rate ratio k_{Me}/k_{Ph} was 0.005 for R′ = Me, but was 1.6−5.3 for bulky groups R′. In the case of **15b** the adjacent *tert*-butyl on the cyclopentadienyl ring would preclude any approach to coplanarity for the phenyl ring in a developing carbocation.

The high dependence of the reaction rate on the solvent polarity and the diverse array of products are readily explained by the process of Scheme 2 with initial ionization to a carbocation (**20**) which can undergo direct or allylic substitution to form **19** or **16a**, elimination to form **17**, or rearrangement to **21** which gives **18**.

An estimate of the reactivity of **15a** relative to 1-methylcyclopentyl trifluoroacetate (**22**) is obtained by multiplying the rate of the corresponding *p*-nitrobenzoate **22**−OPNB of 2.11 × 10^{-9} s^{-1} in 80% acetone at 25 °C[10ab] by the $k_{RO_2CCF_3}/k_{ROPNB}$ rate factor of 5.9 × 10^3 (derived for R = cumyl in MeOH at 25 °C)[7e,10c,d,11a] and the solvent correction factor $k_{1\text{-AdO}_2CCF_3}^{TFE}/k_{1\text{-AdO}_2CCF_3}^{80A}$ of 450[7c,11b] at 50 °C to give a k_{25}^{TFE} (**22**) of 5.6 × 10^{-3} s^{-1}, and a rate ratio, k(**22**)/k(**15a**), of 1.6 × 10^2.

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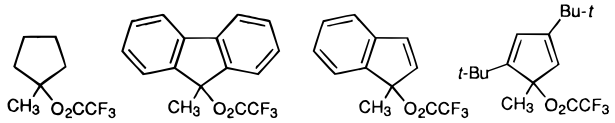
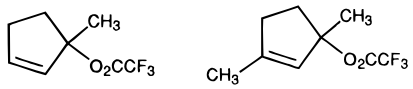
An estimate of the rates of **15a** relative to 9-methyl-9-fluorenyl trifluoroacetate (**23**) and 3-methyl-3-indenyl trifluoroacetate (**24**) is obtained by multiplying the rates of **23**−ODNB and **24**−ODNB in TFE at 25 °C of 1.76×10^{-4} and 2.0×10^{-6} calculated from published[10e] data by the RO_2CCF_3/ROPNB rate factor (above) of 5.9×10^3 to give rate constants of 1.04 and 1.2×10^{-2} s^{-1} for **23** and **24** in TFE at 25 °C, and relative rates for **23**:**24**:**15a** of 3.0×10^4:3.5×10^2:1.0. As discussed below[10a] an allylic methyl group accelerates the solvolysis of an allylic substrate by a factor of 2×10^3, and if the two *tert*-butyl groups in **15a** accelerate the solvolysis by comparable factors, then the reactivities of **23** and **24** relative to that of a derivative of **15a** without these groups would be correspondingly greater.



22 **23** **24** **15a**

Thus, the reactivity of the cyclopentadienyl derivative **15a** is appreciably diminished relative to those of **23** and **24**. Moreover, this substrate is even more unreactive compared to other model compounds. A rate for 3-methyl-3-cyclopentenyl trifluoroacetate (**25**) may be derived from the reported[10a] rate constant for **25**−OPNB in 80% acetone at 25 °C of 1.15 s^{-1}, and the $k_{RO_2CCF_3}/k_{ROPNB}$ and k^{TFE}/k^{80A} rate factors of 5.9×10^3 and 450 noted above to give a k_{25}^{TFE} (**25**) of 3.1×10^6 s^{-1}, and a k(**25**)/k(**15a**) of 9.0×10^{10}. The rate of **15a** would also be significantly enhanced by the allylic *tert*-butyl substituent, as can be noted from the rate factor[10a] $k(CH_3CH{=}CHCMe_2OPNB)/k(CH_2{=}CHCMe_2OPNB)$ of 2.2×10^3 in 80% acetone at 25 °C. Combining these factors gives a predicted rate factor of 2.0×10^{14} for **26**/**15a** in TFE at 25 °C.



25 **26**

Large rate decelerations due to antiaromatic effects have previously been noted in the fluorenyl[5a,10e] and indenyl systems,[5b,10e] which we have estimated as 10^3 and 10^6, respectively, and the effects in the cyclopentadienyl are even more dramatic. The 10^{14} rate depression in TFE at 25 °C for **15a** relative to **26** is truly remarkable, and ranks with the largest of the effects on reactivity due to crowding, strain, and electronic substituent effects. Together these constitute the four major structural effects which have dominating influences on organic reactivity.

In summary the cyclopentadienyl trifluoroacetates **15a** and **15b** are indicated to undergo solvolysis via cyclopentadienyl cation intermediates on the basis of their reaction products, the dependence of their reactivity upon solvent polarity, and the α-Me/α-Ph rate ratio. The reactivity of **15a** is less than that of the cyclopentenyl analogue **26**, by a factor of 10^{14} in TFE at 25 °C, and this enormous difference may be ascribed to the effects of antiaromaticity.

(11) (a) $k_{RO_2CCF_3} = 1.13 \times 10^{-3}$ s^{-1} and $k_{ROPNB} = 1.92 \times 10^{-7}$ s^{-1}; this factor is derived in a more direct fashion than that of 4.5×10^5 reported in ref 7a, and appears preferable for use. (b) A similar average factor of 420 has been derived from measurements of seven different substrates.[10c,d]

(12) (a) Cowell, G. W.; Ledwith, A. *J. Chem. Soc. B* **1967**, 695−697. (b) Brown, H. C.; Dickason, W. C. *J. Am. Chem. Soc.* **1969**, *91*, 1226−1228.

Even though the reactivities of fluorenyl, indenyl, and cyclopentadienyl substrates leading to carbocationic intermediates are enormously depressed relative to model compounds in which antiaromaticity effects are not present, these reactions can nevertheless be carried out at ambient temperatures at reasonable rates. It would appear that the lower limits of reactivity in this series have not yet been reached, and that in particular the carbocationic reactivity of less highly substituted derivatives of **15a** should be observable.

Experimental Section

Reagents and solvents were the best commercial grade available and used as supplied except as indicated. For reactions under an inert atmosphere glassware was flame dried under Ar three times prior to use. Radial chromatography was carried out using a Chromatotron from Harrison Research with silica gel coated plates and solvents as indicated.

2,4-Di-*tert*-butylcyclopentadienone (**13**) was prepared by the reported procedure[6a] and was identified by its ^{1}H NMR spectrum ($CDCl_3$): δ 1.14 (s, 9, *t*-Bu), 1.17 (s, 9, *t*-Bu), 4.98 (d, 1, J = 1.7 Hz, C═CH), 6.53 (d, 1, J = 1.7 Hz, C═CH).

1,3-Di-*tert*-butyl-5-hydroxy-5-methylcyclopenta-1,3-diene (14a). To freshly prepared ketone **13** (1.0 g, 5.4 mmol) in 60 mL of ether in a 100 mL three-neck flask under Ar cooled in dry ice/acetone was added CH_3Li (4 mL, 1.5 M in ether, 6.0 mmol) over 5 min, followed by stirring for 2 h, warming to 25 °C, and stirring overnight. Wet ether was added followed by H_2O and 10 mL of 1 M HCl. The layers were separated, the H_2O layer was washed twice with ether, and the combined ether layers were extracted by H_2O and the brine, dried over $CaSO_4$, and evaporated to give 1.08 g of crude product, which was chromatographed three times (10:90 EtOAc/hexane, R_f = 0.25) to give **14a** (0.427 g, 2.05 mmol, 38%) as a white solid: mp 84−85 °C; IR ($CDCl_3$) 3592 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 9, *t*-Bu), 1.24 (s, 9, *t*-Bu), 1.53 (s, 3, CH_3), 1.56 (s, 1, OH), 5.48 (d, 1, J = 2.0 Hz, CH═C), 5.87 (d, 1, J = 2.0 Hz, C═CH); ^{13}C NMR ($CDCl_3$) δ 23.8, 28.7, 30.8, 31.7, 34.2, 86.1, 123.6, 131.3, 151.7, 161.2; EIMS *m/z* 208 (M^+, 16), 193 ($M^+ - CH_3$, 30), 152 ($M^+ - C_4H_8$, 32), 137 (100), 57 ($C_4H_9^+$, 93); HRMS *m/z* calcd for $C_{14}H_{23}O$ 207.1749, obsd 207.1752; UV λ_{max}^{hexane} 280 nm (ϵ = 1900).

1,3-Di-*tert*-butyl-5-methyl-5-cyclopenta-1,3-dienyl Trifluoroacetate (15a). To a solution of alcohol **14a** (0.345 g, 1.66 mmol) and dry pyridine (0.190 mL, 2.35 mmol) in a 25 mL flask with a magnetic stirrer was added $(CF_3CO)_2O$ (0.440 mL, 3.11 mmol). There was an exothermic reaction and precipitation of solid. After stirring for 15 min, ether was added and the mixture was poured onto ice/water and extracted three times with ether. The combined ether layers were extracted with $NaHCO_3$ solution and brine, dried over $CaSO_4$, and evaporated to give 0.366 g of a yellow liquid containing no **14a** by ^{1}H NMR. Chromatography (5:95 EtOAc/hexane, R_f = 0.62) gave **15a** (0.269 g, 0.885 mmol, 53%) as a pale yellow liquid: IR ($CDCl_3$) δ 1778 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9, *t*-Bu), 1.21 (s, 9, *t*-Bu), 1.74 (s, 3, CH_3), 5.75 (d, 1, J = 2.0 Hz, C═CH), 6.06 (d, 1, J = 1.9 Hz, C═CH); ^{13}C NMR ($CDCl_3$) 21.8, 28.5, 30.5, 31.6, 34.1, 95.3, 114.3 (q, $^1J_{CF}$ = 287 Hz, CF_3), 124.5, 126.5, 154.9, 155.5 (q, $^2J_{CF}$ = 42 Hz, $COCF_3$), 156.8; ^{19}F NMR ($CDCl_3$) δ −75.75; UV λ_{max}^{hexane} 277 nm (ϵ = 2900); EIMS *m/z* 304 (M^+, 6), 289 ($M^+ - CH_3$), 57 ($C_4H_9^+$, 100); HRMS *m/z* calcd for $C_{16}H_{23}O_2F_3$ 304.1650, obsd 304.1636.

Trifluoroethanolysis of 15a. In a preparative reaction **15a** (0.170 g, 0.558 mmol) in 25 mL of CF_3CH_2OH with 2,6-lutidine (0.130 mL, 1.12 mmol) was heated at 46 °C for 250 min. The solution was added to 12 mL of H_2O and extracted five times with pentane, and the pentane from the combined organic layers was removed by slow distillation. The crude product was chromatographed with hexane to give five products, of which the first (trace) in order of elution was unidentified and the others were identified as **16**−**19**, respectively, in order of elution, in a ratio of 66:10:14:10, as determined from the ^{1}H NMR of the crude product.

2,5-Di-*tert*-butyl-3-methyl-5-cyclopenta-1,3-dienyl 2,2,2-Trifluoroethyl Ether (16a): ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9, *t*-Bu), 1.19 (s, 9,

t-Bu), 2.07 (d, 3, J = 1.9 Hz, CH_3C═C), 3.50 (q, 2, J_{HF} = 9.9 Hz, CH_2CF_3), 5.62−5.73 (m, 2, 2CH═C); ^{13}C NMR ($CDCl_3$) δ 17.1, 26.1, 29.7, 33.2, 36.2, 61.4 (q, $^2J_{CF}$ = 33.9 Hz, CH_2CF_3), 93.5 124.5, (q, $^1J_{CF}$ = 278 Hz), 128.6, 134.0, 144.9, 157.7; ^{19}F NMR ($CDCl_3$) δ −75.37 (t, J_{HF} = 9 Hz); UV λ_{max}^{hexane} 271 nm (ϵ = 930); EIMS *m/z* 290 (M^+, 7), 275 ($M^+ - CH_3$, 4), 234 ($M^+ - C_4H_8$, 33), 219 ($M^+ - C_5H_{11}$, 73), 178 (22), 57 ($C_4H_9^+$, 100); HRMS *m/z* calcd for $C_{16}H_{25}OF_3$ 290.1858, obsd 290.1862.

1,3-Di-*tert*-butyl-5-methylene-1,3-cyclopentadiene (17): ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 9, *t*-Bu), 1.15 (s, 9, *t*-Bu), 5.61 (d, J = 1.8 Hz, C_4H), 5.65 (br s, 1, C*H*H), 5.86 (br s, 1, C*H*H), 6.13 (t, 1, C_2H), assignments confirmed by the ^{1}H,^{13}C-heteronuclear coupled spectrum (2D HMQC); ^{13}C NMR ($CDCl_3$) δ 29.2, 31.96, 32.02, 33.09, 116.6 (d, $^1J_{CH}$ = 161.8 Hz, C_4), 119.6 (t, $^1J_{CH}$ = 158.1 Hz, CH_2), 128.1 (d, J = 161.8 Hz, C_2), 146.6, 151.0, 155.9; UV λ_{max}^{hexane} 246 (ϵ = 15 000), 370 (ϵ = 420) nm; EIMS *m/z* 190 (M^+, 40), 175 ($M^+ - CH_3$, 100), 133 ($M^+ - C_4H_9$, 87), 119 ($M^+ - C_5H_{11}$, 50), 57 ($C_4H_9^+$, 52); HRMS *m/z* calcd for $C_{14}H_{22}$ 190.1722, obsd 190.1725.

3,5-Dimethyl-2-*tert*-butyl-5-[2′-(2″,2″,2″-trifluoroethoxy)-2′-propyl]-1,3-cyclopentadiene (18): ^{1}H NMR ($CDCl_3$) δ 1.106 (s, 3, CH_3), 1.114 (s, 6, CMe_2), 1.178 (s, 9, *t*-Bu), 2.05 (d, 3, J = 1.5 Hz, CH_3C═C), 3.73 (q, 2, J_{HF} = 8.7 Hz, CH_2CF_3), 5.87 (d, 1, J = 1.4 Hz, CH═C), 5.92 (m, 1, C═CH); ^{13}C NMR ($CDCl_3$) δ 16.4, 17.2, 21.2, 29.7, 29.8, 32.8, 59.2, 60.7 (q, $^2J_{CF}$ = 33.7 Hz), 79.1, 124.4 (q, $^1J_{CF}$ = 278 Hz), 135.4, 140.5, 140.8, 153.6; ^{19}F NMR ($CDCl_3$) δ −75.1 (t, J_{HF} = 8.5 Hz); UV λ_{max}^{hexane} 246 nm (ϵ = 2000); EIMS *m/z* 290 (M^+, 3), 219 (7), 150 (5), 141 ($CF_3CH_2OCMe_2^+$, 100); HRMS *m/z* calcd for $C_{16}H_{25}F_3O$ 290.1858, obsd 290.1847.

1,3-Di-*tert*-butyl-5-methyl-5-cyclopenta-1,3-dienyl 2,2,2-Trifluoroethyl Ether (19): ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9, *t*-Bu), 1.21 (s, 9, *t*-Bu), 1.55 (s, 3, Me), 3.50 and 3.51 (ea q, 1, J_{HF} = 8.9 Hz, CH_2CF_3), 5.35 (bd, 1, J = 1.6 Hz, C═CH), 6.05 (d, 1, J = 2.0 Hz, C═CH); ^{13}C NMR ($CDCl_3$) δ 22.7, 28.7, 30.6, 31.9, 33.8, 61.8 (q, $^2J_{CF}$ = 34 Hz), 90.8, 124.3 (q, $^1J_{CF}$ = 278 Hz), 126.8, 127.4, 154.5, 157.9; ^{19}F NMR ($CDCl_3$) −74.6 (t, J = 8.9 Hz); UV λ_{max}^{hexane} 273 nm (ϵ = 2000); EIMS *m/z* 290 (M^+, 10), 275 ($M^+ - CH_3$, 22), 234 ($M^+ - C_4H_8$, 43), 219 ($M^+ - C_5H_{11}$, 58), 141 (34), 57 ($C_4H_9^+$, 100); HRMS *m/z* calcd for $C_{16}H_{25}F_3O$ 290.1858, obsd 290.1860.

In a separate experiment a solution of **15a** (3.5 mg, 0.0115 mmol) and 2,6-lutidine (2.7 μL, 0.023 mmol) in 1 g of CF_3CD_2OD in an NMR tube was monitored by ^{1}H NMR and showed a half-life for reaction of about 47 min, and after 247 min showed no residual **15a**. The reaction mixture was poured into water and extracted with ether which was dried and evaporated, and the product was chromatographed (5:95 EtOAc/hexane) and analyzed by GC/MS to give peaks with the following retention times (min), with identification as shown (*vide infra*) based on their MS patterns: 7.9 (unidentified, but probably **16b**, as ions at *m/z* 236 ($M^+ - C_4H_8$), 221 (M^+, $- C_5H_{11}$), and 57 ($C_4H_9^+$) were present), 7.97 (**19**), 8.03 (**17**), 8.13 (**16a**), and 8.75 (**18**).

The alcohol **14a** was not observed in any of the product studies, and was shown to be stable under the reaction conditions.

Ethanolysis of 15a. A solution of **15a** (6.4 mg, 0.0211 mmol) in 0.65 mL of EtOH-d_6 with 2,6-lutidine (5 μL, 0.043 mmol) in an NMR tube was heated at 100 °C and monitored by ^{1}H NMR. During the reaction the ratio of the products formed showed some variation with time, but after 6.5 h **15a** had disappeared and the ratio of products appeared constant. The reaction mixture was poured into H_2O and pentane, the aqueous layer was extracted five times with pentane, and the combined organic layers were dried and evaporated, and by analogy with the product from trifluoroethanolysis of **15a** appeared by ^{1}H NMR to contain the ether **16**, fulvene **17**, and the ether **19** in a ratio of 42:40:18. No signals corresponding to those of **18** were detected. Analysis of the products by GC/MS showed 5% unreacted starting material and the products **16a**, **17**, **18**, and **19** ($R^1 = C_2D_5$) in relative percentages of 43, 32, <1, and 17%, respectively, in good agreement with the NMR results. In addition a signal corresponding to 3% of the total, and with a fragmentation pattern similar to **16a**, was observed, which may be **16b**. The presence of 3% **16b** in the product mixture could not be excluded on the basis of the ^{1}H NMR. The products were identified by comparison of their EIMS peaks to those for the corresponding products from trifluoroethanolysis, as follows: (**16a**) *m/z* 241 (M^+, 19), 226 ($M^+ - CH_3$, 22), 185 ($M^+ - C_4H_8$, 48), 170 ($M^+ - C_5H_{11}$, 100), 152 (90), 57 ($C_4H_9^+$, 92); (**16b**) *m/z* 241 (M^+, 13), 226 (4), 185 (49), 170 (100), 152 (64), 57 (55); (**17**) *m/z* 192 ($M^+ + 2$, 5), 191 ($M^+ + 1$, 42), 190 (M^+, 11), 177 ($M^+ - CH_3 + 2$), 176 ($M^+ - CH_3 + 1$, 99), 175 ($M^+ - CH_3$, 59); 135 ($M^+ - C_4H_7$, 45), 134 ($M^+ - C_4H_8$, 100), 133 ($M^+ - C_4H_9$, 66), 57 ($C_4H_9^+$, 66); (**18**) *m/z* 134, 119, 92 (C_2D_5-$OCMe_2^+$), 57 (*t*-Bu^+); (**19**) *m/z* 241 (M^+, 16), 226 ($M^+ - CH_3$, 26), 185 ($M^+ - C_4H_8$, 49), 170 ($M^+ - C_5H_{11}$, 81), 152 (63), 57 ($C_4H_9^+$, 100).

1,3-Di-*tert*-butyl-5-hydroxy-5-phenylcyclopenta-1,3-diene (14b). As described for **14a** the reaction of **13** (0.279 g, 1.45 mmol) with PhLi (0.9 mL, 1.8 M in cyclohexane/ether, 1.62 mmol) gave 0.290 g of an oil which by ^{1}H NMR contained 50% of the desired product. Chromatography (5:95 EtOAc/hexane, R_f = 0.25) gave **14b** (0.080 g, 0.03 mmol, 20%) as a pale yellow oil: IR ($CDCl_3$) 3601 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 9, *t*-Bu), 1.13 (s, 9, *t*-Bu), 1.95 (brd s, 1, OH), 5.62 (d, 1, J = 1.9 Hz, CH═C), 6.05 (d, 1, J = 2.1 Hz, CH═C), 7.1−7.4 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ 28.7, 30.8, 32.0, 34.4, 89.4, 124.8, 125.2, 126.2, 127.9, 133.0, 140.4, 153.0, 163.8; EIMS *m/z* 270 (M^+, 50), 255 ($M^+ - CH_3$, 91), 214 ($M^+ - C_4H_8$, 56), 199 ($M^+ - C_5H_{11}$, 94), 158 (48) , 57 ($C_4H_9^+$, 100); HRM S *m/z* calcd for $C_{19}H_{26}O$ 270.1984, obsd 270.1991.

1,3-Di-*tert*-butyl-5-phenyl-5-cyclopenta-1,3-dienyl Trifluoroacetate (15b). As described for **15a** the reaction of **14b** (22 mg, 0.082 mmol) with pyridine (8 μL, 0.1 mmol) and $(CF_3CO)_2O$ (44 μL, 0.31 mmol) gave after chromatography (10:90 EtOAc/hexane, R_f = 0.6) **15b** (20 mg, 0.053 mmol, 65%) as a clear liquid: IR ($CDCl_3$) 1789 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 9, *t*-Bu), 1.17 (s, 9, *t*-Bu), 5.78 (d, 1, J = 2.0 Hz, CH═C), 6.24 (d, 1, J = 2.0 Hz, CH═C), 7.2−7.4 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ 28.5, 30.3, 32.2, 34.3, 97.2, 114.3 (q, $^1J_{CF}$ = 287 Hz), 124.4, 127.2, 127.4, 128.37, 128.44, 135.4, 154.3 (q, $^2J_{CF}$ = 42 Hz), 155.9, 158.7; ^{19}F NMR ($CDCl_3$) δ −75.3; EIMS *m/z* 366 (M^+, 10), 310 ($M^+ - C_4H_8$, 40), 57 ($C_4H_9^+$, 100); HRMS *m/z* calcd for $C_{21}H_{25}F_3O_2$ 366.1807, obsd 366.1818.

Trifluoroethanolysis of 15b. As for **15a** a solution of **15b** (12 mg, 0.032 mmol) in 0.6 mL of CF_3CD_2OD was heated to 61 °C for 2 h. After workup 1.9 mg of material was obtained which by mass spectral analysis contained unreacted **15b** or an isomer (EIMS *m/z* 366 (M^+)) and substitution product derived from **15b** ($R^1 = CF_3CH_2$) (EIMS *m/z* 354 (M^+), 298 ($M^+ - C_4H_8$)).

Kinetic Measurements. Kinetics were measured using Perkin-Elmer Lambda 12 and Varian 210 spectrophotometers using the general procedures and solvent preparation as reported previously.[5] In a typical procedure solutions of **15a** (2 μL, 0.118 M in CH_3CN) and 2,6-lutidine (4 μL, 0.118 M in CH_3CN) were added to 1.2 mL of 97% TFE, and the decrease in absorbance (ΔA = 0.1) was monitored at 300 nm. Stable end points were observed, with an isobestic point at 335 nm and a final λ_{max} at 375 nm, primarily due to fulvene **17**. In the absence of buffer the end point was not stable, and the rates were measured using 0.1−0.25 times the concentration of **15a** used in the presence of 2,6-lutidine. For measurements of **15b** a solution of the substrate (4 μL, 0.01 M in CH_3CN) was added to 1.2 mL of 97% TFE, and the increase in absorbance was monitored at 272 nm (ΔA = 0.05). For reactions in HFIP the concentrations of **15b** were 2−5 times larger.

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Supporting Information Available: ^{1}H NMR spectra (8 pages). See any current masthead page for ordering and Internet access instructions.

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