## BIS(2,6-DIFLUOROPHENYL)BENZOYLMETHYL CATION: $\alpha$ -KETOCARBENIUM ION AS A SINGLE-ELECTRON ACCEPTOR

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Summary: The title carbenium ion 1 was observed by low temperature NMR in solution. Its strong oxidizing power was demonstrated by the reduction potential and the effective oxidation of methoxy-substituted benzopinacolone 3.

In recent years, much attention has been paid to carbenium ions with strong electronwithdrawing substituents, most notably those ions containing the carbonyl group.<sup>1,2</sup> Although the electrophilic nature of  $\alpha$ -carbonylcarbenium ions is well-known, their ability to act as single-electron acceptors was unknown until the discovery of the oxidizing ability of Ph<sub>2</sub>C<sup>-</sup>-COPh.<sup>1b,c</sup> However, this cation readily undergoes intramolecular cyclization to 2,3-diphenylbenzofuran,<sup>1c,2c</sup> making the observation of a clean oxidation difficult.



This side reaction can be suppressed by protecting the phenyl rings adjacent to the cation center with suitable substituents. We now wish to report the preparation of such a long-lived  $\alpha$ -ketocarbenium ion,  $(2,6-F_2C_6H_3)_2\dot{C}-COPh$  (1). As an indication of its strong oxidizing ability, the reaction of the cation 1 with an electron-rich molecule is also examined.

The  $\alpha$ -keto cation 1 was generated as a deep reddish purple solution by adding 1.5 equivalents of AgSbF<sub>6</sub> to a methylene chloride solution of bromoketone  $2^3$  at -78 °C. The structure of 1 was characterized by <sup>13</sup>CNMR spectroscopy<sup>6</sup> using the <sup>13</sup>C(90%)-labeled samples,



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 $(2,6-F_2C_6H_3)_2^{13}\dot{C}$ -COPh and  $(2,6-F_2C_6H_3)_2\dot{C}^{-13}$ COPh. Their spectra exhibited enhanced signals at 209.2 ppm ( $^{13}\dot{C}$ ) and 196.5 ppm ( $^{13}C$ =O), respectively. These values are larger by ca. 4 ppm than the chemical shifts of the parent cation Ph<sub>2</sub>\dot{C}-COPh (C<sup>+</sup> 205.4 and C=O 192.0 ppm).<sup>1</sup>

The cation 1 is stable in methylene chloride at -72 °C for at least 5 h. When warmed to -30 °C, it decomposed within 20 minutes to give a complex mixture of products (>7 components). In the presence of anisole, cation 1 reacts instantly at -78 °C to give the para-alkylation product,  $(2,6-F_2C_6H_3)_2AnC-COPh$ ,<sup>5</sup> (An = *p*-methoxyphenyl) in 48% yield.

The cyclic voltammogram of 1<sup>7</sup>, quickly recorded at -30 °C, showed an irreversible reduction wave with a peak potential ( $E_p^{red}$ ) of +0.72 V vs. Ag/Ag<sup>+</sup>. This value indicates that 1 is a much more powerful oxidant than either Ce<sup>4+</sup> ( $E_p^{red}$  +0.64 V<sup>1c</sup>), a typical single-electron oxidizing agent, or Ph<sub>2</sub>C<sup>+</sup>-COPh ( $E_p^{red}$  +0.52 V<sup>1c</sup>).

The high oxidizing ability of 1 was demonstrated by the effective oxidation of the electron-rich benzopinacolone,  $An_3C$ -COAn (3).  $AgSbF_6$  (0.34 mmol) was added to a refluxing solution of 2 (0.35 mmol) and 3 (0.35 mmol) in 1,2-dichloroethane (7.0 ml). The reaction mixture was heated at reflux for 15 minutes, after which an aqueous work-up followed. The oxidation products,  $An_3COH$  and AnCOOH, were separated by TLC and isolated in 84 and 83% yields, respectively. The reduction product, (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>CH-COPh, was isolated in 85% yield. The alcohol,

Scheme 1 (An = p-MeOC<sub>6</sub>H<sub>4</sub>, **C** = 90% <sup>13</sup>C)



 $(2,6-F_2C_6H_3)_2C(OH)$ -COPh,<sup>5</sup> was also isolated (15% yield) and would appear to be the result of hydration of 1 by traces of water present in the reaction mixture. Despite the instability of 1 at high temperatures, no decomposition products from 1 were detected, indicating that the oxidation is quite clean and very effective.<sup>8</sup>

We have previously found<sup>9</sup> that the pinacolone **3** undergoes single-electron oxidation by  $Ce^{4+}$  to give the transient radical cation **3**<sup>+°</sup>, which rapidly splits into  $An_3C^+$  and  $An\dot{C}O$ . It appears likely that the oxidation by **1** proceeds in a similar fashion via the single-electron transfer pathway shown in Scheme 1. In this reaction sequence, the radical,  $(2,6-F_2C_6H_3)_2\dot{C}-COPh$ , is able to accept another electron from An $\dot{C}O$  (or from **3**), resulting in a net two-electron oxidation. The overall reaction yields  $An_3C^+$ ,  $An\dot{C}O$ , and  $(2,6-F_2C_6H_3)_2\dot{C}-COPh$  in a ratio of 1:1:1.

This mechanism is supported by the CIDNP experiment. When the reaction was carried out in a <sup>13</sup>C NMR probe with <sup>13</sup>C-labeled **3** (An<sub>3</sub><sup>13</sup>C – <sup>13</sup>COAn), intense emission peaks were observed at 162.2 and 168.4 ppm during the initial 15 minutes (Fig. 1). These signals correspond to the labeled carbons of An $\dot{C}O^{10}$  and AnCOOH, respectively. As heating continued, both emission peaks gradually disappeared with the development of the normal absorption peak of AnCOOH. These observations indicate the involvement of a radical species as a precursor to An $\dot{C}O$  and AnCOOH, which is consistent with the suggested reaction sequence, i.e. single-electron oxidation of An $\dot{C}O$  and subsequent hydration by traces of water.

Whereas the  $\alpha$ -carbonyl substituent significantly destabilizes carbenium ions, it tends to stabilize radicals.<sup>11</sup> Therefore, the unusually strong oxidizing power of the cation 1 can be attributed to an increase in the energy difference between 1 and the corresponding radical due to the presence of an  $\alpha$ -carbonyl group.



Fig.1. <sup>13</sup>C NMR spectrum of the reaction mixture from An<sub>3</sub>C-COAn (0.1 M), 2 (0.1 M), and AgSbF<sub>6</sub> (0.1 M) in CICH<sub>2</sub>CH<sub>2</sub>CI-CDCI<sub>3</sub> (9:1) after heating at 75 °C for 2.5 min; C = 90% <sup>13</sup>C.

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**References and Notes** 

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- To obtain the bromoketone 2, (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>CHOH<sup>4</sup> was reduced in 90% yield to (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>CH<sub>2</sub><sup>5</sup> with P/I<sub>2</sub> in acetic acid–water and then benzoylated with BuLi/PhCOCI in THF– HMPA (9:1) to give (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>CH–COPh<sup>5</sup> in 64% yield. This compound was then brominated by Br<sub>2</sub>/DBU in CCl<sub>4</sub> to give 2<sup>5</sup> in 61% yield.
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- The following new compounds were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis: (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>CH<sub>2</sub> (mp. 68–69 °C), (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>CH-COPh (mp. 164–165 °C), (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>CBr-COPh (**2**) (mp. 132.5–133.5 °C), (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>AnC-COPh (mp. 138–139 °C), (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C(OH)-COPh (mp. 144–145 °C).
- 6. The solvent was transferred *in vacuo* from P<sub>2</sub>O<sub>5</sub> to a chilled (liquid N<sub>2</sub>) NMR tube containing **2** and AgSbF<sub>6</sub> to avoid contamination by water. The resulting frozen mixture was sealed under vacuum and warmed to -78 °C.
- The cyclic voltammetry of 1 was conducted in methylene chloride by using tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. The voltammogram was recorded 2 minutes after generation of 1 at a scan rate of 0.1 Vs<sup>-1</sup>.
- 8. Under the same conditions  $Ph_2C+COPh$  oxidizes **3** in only ~20% yield.
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