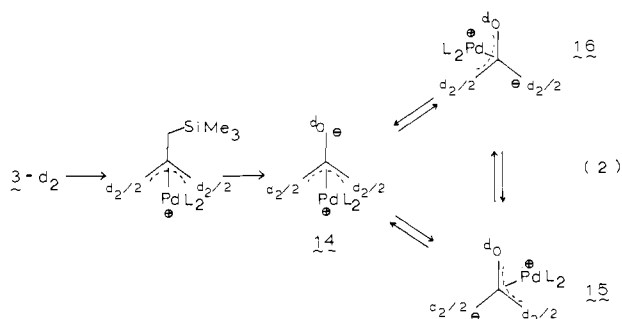


The above results are consistent with TMM-PdL<sub>2</sub> being unsymmetrical as represented by **2** and in eq 2, in direct contradiction to the case of iron. With a very reactive trap, such



as the highly acidic sulfone ester, the kinetically produced complex **14** protonates faster than it isomerizes. With a less acidic trap, such as benzalacetone, **14** lives longer and allows a palladium migration. A 1,2-migration to **15** and/or **16** effectively scrambles all three methylene groups.  $\alpha,\beta$ -Unsaturated carbonyl compounds represent kinetically slow traps; thus, equilibration overwhelms cycloaddition. Such experimental observations supported by calculations indicate the nucleophilic character of all the methylene carbons of **2** and rationalize the total failure of simple alkyl-substituted olefins (even strained ones) as well as electron-rich olefins to react with TMM-PdL<sub>2</sub>.<sup>10</sup> It is noteworthy that although palladium can easily adopt a coordinatively saturated configuration in such complexes it prefers to exist as a  $\eta^3$  **16** species. This study suggests caution must be exercised in the interpretations regarding the structure of other TMM-metal complexes and that the case of iron cannot be simply extrapolated to other metals.

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(10) However, reaction of methylenecyclopropanes and olefins catalyzed by palladium is reported to go through TMM complexes (see ref 6). Unfortunately, the available data does not distinguish between a direct co-oligomerization reaction (cf. ref 3 and Noyori, R.; Ishigami, T.; Hayashi, N.; Takaya, H. *J. Am. Chem. Soc.* 1973, 95, 1674) and reaction through TMM.

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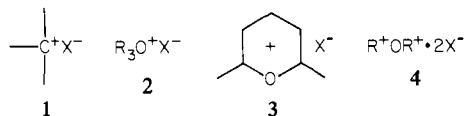
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### Preparation and Characterization of Novel Dication Ether Salts: Ar<sup>+</sup>OAr<sup>+</sup>·2CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>

Sir:

Carbocations (**1**) are among the most common and extensively investigated reactive intermediates.<sup>1</sup> Besides direct spectral observation,<sup>2</sup> generally in superacidic media, numerous carbocations



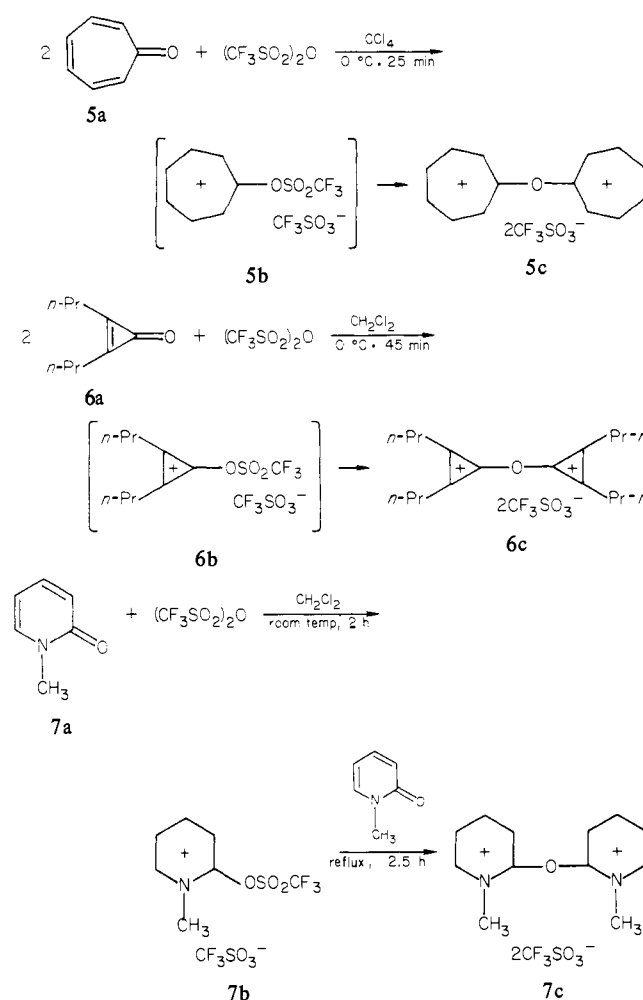
have been isolated as stable crystalline salts.<sup>3</sup> Similarly, oxonium

(1) Olah, G. A.; Schleyer, P. v. R., Eds. "Carbocation Ions", Wiley-Interscience: NY, 1968-1976; Vol. I-V.

(2) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Science (Washington, D.C.)* 1979, 206, 13-20, and references therein.

(3) Sundaralingam, M.; Chwang, A. K. In "Carbocation Ions"; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley-Interscience: NY, 1976; Vol. V, pp 2427-2476.

### Scheme I



(**2**) as well as pyrylium (**3**) ions are well-established organic species.<sup>4</sup> In contrast, carbocations linked by an oxygen, namely, dication ethers (**4**), are to date unknown. Hence, in this communication, we report the serendipitous preparation of such novel dication ether salts in good yield by a single-step reaction.

Addition of 6.0 mmol of pure (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>O to a magnetically stirred solution of 10 mmol of tropone in 20 mL of anhydrous CCl<sub>4</sub> under an Ar atmosphere at 0 °C results in a colorless crystalline precipitate. Filtration under rigorously anhydrous conditions and recrystallization from anhydrous CH<sub>3</sub>CN and ether gave 97% of **5c**. Similarly, 4 mmol of cyclopropenone **6a** and 2 mmol of (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> gave **6c** which could only be characterized in solution. There is little doubt that these reactions proceed through the intermediacy of the respective monocations **5b** and **6b** as shown in Scheme I, but in no case were these intermediates isolable, even with inverse addition to a large excess of anhydride. In contrast, addition of 20 mmol of *N*-methyl-2-pyrindone in 15 mL of dry CH<sub>2</sub>Cl<sub>2</sub> to 20 mmol of anhydride in 15 mL of dry CH<sub>2</sub>Cl<sub>2</sub> resulted, after 2 h at room temperature and subsequent addition of 20 mL of anhydrous ether, in 6.1 g (77%) of crude monocation **7b**. Recrystallization from anhydrous CH<sub>2</sub>Cl<sub>2</sub>/ether gave pure **7b**. Subsequent reaction of monocation **7b** with an additional equivalent of pyridone **7a** in refluxing CH<sub>2</sub>Cl<sub>2</sub> gave after 2.5 h 74% of dication **7c**.

Compounds **5c-7c** as well as **7b** were characterized by chemical and spectral means as summarized in Table I. In particular, all dications as well as monocation **7b** are extremely hygroscopic and yield upon exposure to moisture either the expected respective hydroxy cations **5d-7d** and/or the starting ketone, depending upon the exact reaction conditions. The identity of the hydrolysis

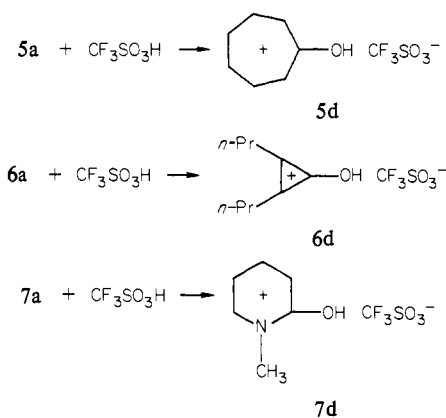
(4) Perst, H. In "Carbocation Ions"; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley-Interscience: NY, 1976; pp 1961-2047.

Table I. Physical and Spectral Data for Compounds 5c-7c and 7b

compd	% yield	mp, °C	mol wt		IR, <sup>a</sup> cm <sup>-1</sup>	NMR		
			calcd	expt		<sup>19</sup> F, <sup>b</sup> δ	<sup>1</sup> H, <sup>c</sup> δ	<sup>13</sup> C, <sup>c</sup> δ
5c	97	154 (dec)	494.4	491	1470 (s), 1300 (s), 1263 (s), 1227 (s), 1199 (s), 1160 (s), 1036 (s), 1030 (s)	87.1	8.98-9.58 (m)	145.8, 154.7, 155.9, 174.2
6c <sup>d</sup>			558.6	552		87.1	1.12 (t, <i>J</i> = 7.5 Hz), 1.94 (sext, <i>J</i> = 7.5 Hz), 3.13 (t, <i>J</i> = 7.5 Hz)	13.1, 18.3, 28.1, 161.3, 165.2, [113.2, 117.4, 121.7, 126.0, CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup> ]
7b	77	66-67	391.3	400	1635 (s), 1580 (m), 1441 (s), 1462 (sh), 1285-1260 (s br), 1229 (s), 1173 (s), 1133 (s), 1042 (s), 1033 (s), 905 (m)	87.3, 93.8	4.26 (s, 3 H), 7.96-8.16 (m, 2 H), 8.62-8.88 (m, 2 H)	45.2, 120.1, 127.6, 148.4, 150.6, 157.5, [110.0, 112.8, 125.5, 138.2 coval CF <sub>3</sub> SO <sub>3</sub> ], [102.6, 115.3, 128.0, 140.7 ionic CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup> ]
7c	74	185-186	500.4	506	1640 (m), 1579 (m), 1508 (s), 1468 (m), 1305 (m), 1280-1250 (s br), 1228 (s), 1183 (s), 1160 (s), 1038 (s), 1030 (s), 905 (m)	87.1	4.32 (s, 6 H), 7.80-8.03 (m, 4 H), 8.51-8.83 (m, 4 H)	44.5, 117.4, 125.8, 147.2, 150.8, 155.2, [115.4 and 128.1 inner lines of CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup> quart]

<sup>a</sup> All in Nujol mull except 7c in KBr pellet. <sup>b</sup> All in CD<sub>3</sub>CN except 6c in CDCl<sub>3</sub>. All relative to C<sub>6</sub>F<sub>6</sub>. <sup>c</sup> All in CD<sub>3</sub>CN except 6c in CDCl<sub>3</sub>. All relative to Me<sub>4</sub>Si. <sup>d</sup> 6c was characterized in solution only; evaporation of the solvent leaves an oil contaminated with minor impurities.

## Scheme II



products was easily confirmed by means of authentic samples<sup>5</sup> of **5d-7d** prepared by reaction of the respective ketones with 1 equiv of trifluoromethanesulfonic acid as shown in Scheme II. Molecular weight determinations were carried out by means of simple titration with dilute aqueous NaOH and are in excellent agreement with calculated values for both the dications **5c-7c** and the monocation **7b**.

Further structural proof is provided by the spectral data in Table I. Particularly significant is the fact that, as expected, the monocation **7b** shows two distinct fluorine absorptions by <sup>19</sup>F NMR whereas the dications **5c-7c** all show a single fluorine absorption, in the region of ionic<sup>6</sup> CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, as required. Both the proton and carbon-13 NMR spectra show significant downfield shifts for the dications compared to their respective starting ketones as expected for such electron-deficient species. The proton as well as carbon-13 NMR spectra of dications **5c-7c** are in good agreement with literature values of model compounds such as the 1-ethoxy-2,3-di-*n*-propylcyclopropenium cation,<sup>7</sup> the tropylium cation,<sup>8</sup> and the *N*-methyl-3-hydroxypyridinium ion.<sup>9</sup> Field-desorption mass spectra of ions **5c**, **7c**, and **7b** are consistent with the proposed structures as well.<sup>10</sup>

(5) Hydroxy cations **5d-7d** have physical and spectral properties in accord with their proposed structures.

(6) KOSO<sub>2</sub>CF<sub>3</sub> in CD<sub>3</sub>CN shows a fluorine signal at 87.4 ppm whereas the "covalent triflate" in (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>O appears at 91.7 ppm (CDCl<sub>3</sub>, relative to C<sub>6</sub>F<sub>6</sub>).

(7) Dehmlov, E. V.; Zeisberg, R.; Dehmlov, S. S. *Org. Magn. Reson.* **1975**, *7*, 418-421.

(8) Spiessicke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468-472.

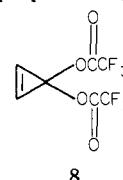
(9) Takeuchi, Y.; Dennis, N. *Org. Magn. Reson.* **1976**, *8*, 21-27.

(10) Complete details of the mass spectra will be given in the full paper or in a separate publication.

The simplicity of both the <sup>1</sup>H and <sup>13</sup>C NMR spectra at room temperature suggests that these dications are freely rotating rather than perpendicular (pseudoallene structure) about the C-O-C bond. Theoretical calculations<sup>11</sup> at the STO-3G level predict a rotational barrier of about 6 kcal/mol, with the planar form being preferred for the parent dicyclopropenyl ether dication, indicating a free rotor at room temperature, as required by the spectral data.

The only other reaction known so far which leads to a dication linked by an oxygen atom is the reaction of triflic anhydride with triphenyl phosphinioxides, yielding diphosphonium salts.<sup>12</sup>

The unique character of these reactions is further underlined by the facts that cyclopropenone reacts with trifluoroacetic anhydride to give the cyclopropenone 3,3-trifluoroacetate **8**<sup>13</sup> only



and that alkoxy cyclopropenyl cations apparently show no tendency to eliminate the -OR group by reaction with a second mole of the cyclopropenone.<sup>14</sup>

In summary, we have discovered a simple direct means of preparing novel dication ethers **5c-7c**. These ions are remarkably stable salts that are easily isolated and handled in the absence of all moisture and strongly nucleophilic solvents or reagents. Experimental as well as theoretical data<sup>11</sup> indicate a planar free rotor structure for these ions. The full scope of such dication ether salt generation as well as the chemistry of these novel dications will be the subject of future papers.

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